# ncasi technical bulletin

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 10016

# USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY:

# THE 104 MILL STUDY

TECHNICAL BULLETIN NO. 590

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Technical Bulletin No. 590

## USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY: THE 104 MILL STUDY

In March 1988, EPA and the paper industry jointly released the results of a screening study that provided information on the formation and release of 2378-TCDD and 2378-TCDF from bleached kraft pulp mills. This screening study of five U.S. mills indicated that the bleaching process was responsible for the formation of the trace levels of TCDD/TCDF previously detected in mill exports.

At the conclusion of the screening study, the U.S. paper industry indicated its willingness to undertake further studies into (a) the mechanisms of TCDD/TCDF formation in pulp bleaching and (b) means to reduce generation and release and to pursue these efforts in cooperation with EPA. While EPA endorsed the concept of this type of research, it also expressed a strong desire for a comprehensive inventory of releases from all 104 U.S. chemical pulp mills which practice chlorine based bleaching.

Accordingly, the industry entered into a voluntary agreement to generate TCDD/TCDF data on the export vectors (pulp, final effluent and wastewater treatment sludges) of all bleached pulp mills in the U.S. and to provide data on process operating conditions during the sampling periods. Certain ancillary studies (e.g. full congener analyses on a limited number of samples and an inter-laboratory comparison study) were also provided for in the cooperative study agreement. A copy of the agreement is included as Appendix A of this report.

At the same time, the industry determined to pursue its original intention to carry out detailed studies of mechanisms and locations of TCDD/TCDF formation in the bleaching process. The full scale mill sampling portion of this effort became known as the 'Intensive Study' and will be cover in the next Technical Bulletin in this series.

This report presents the results of the cooperative screening study called for under the industry's agreement with EPA. It is important to recognize that the data reported here actually reflect a 'snapshot in time' of the releases from each mill operating under its own set of process conditions. This means that the results are not well suited to attempts to infer relationships between process operating conditions and TCDD/TCDF formation rates; conditions that may vary from mill to mill are not all covered by the process data collected.

The 'snapshot' nature of the sampling also means that results generated during the time period covered by this study (mid 1988 through mid 1989) do not reflect formation and release rates being achieved by the industry now or in the future. The industry has voluntarily undertaken extensive efforts to reduce the formation of TCDD/TCDF in its bleaching operations. In many cases these efforts have already achieved substantial reductions (as noted in Appendix F) and in others results will not be available until process changes are fully implemented.

This report first reviews the major features of the study design, sample collection, and analytical methodologies. The significant findings from the study are presented and discussed by export vector. The discussion focuses on a presentation of the mass discharge of 2378-TCDD and 2378-TCDF and their relative distribution in the three export vectors. Attempts at correlating the mass discharged to bleach plant and waste treatment operating variables were generally unsuccessful and beyond the scope of the study design.

This bulletin was prepared by Dr. Ray C. Whittemore, Research Engineer, at NCASI Northeast Regional Center. Dr. Whittemore was also responsible for preparing guidance for sample collection, process data collection and submittals to EPA, and reporting of analytical results to EPA and the industry. The analytical parts of the study were managed by Larry Lafleur, Organio Analytical Program Manager, and Terry Bousquet, Research Chemist, both at NCASI's West Coast Regional Center.

NCASI would also like to thank the industry personnel who assisted staff in the sampling effort and data review process.

Question and comments on this bulletin are solicited and should be directed to Dr. Whittemore, at the Northeast Regional Center, Tufts University, Medford, MA 02155 (617) 381-3254, or to this office (212) 532-9001.

Very truly yours,

Isaiah Gellman

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# USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY: THE 104 MILL STUDY

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ABSTRACT : In March of 1988, the U.S. EPA and the U.S. pulp and paper industry released the results of a five mill screening study that provided some of the first comprehensive results on the formation and discharge of chlorinated dibenzodioxins (CDDs) and dibenzofurans (CDFs) from bleached kraft mills. This early study confirmed that the bleaching process was primarily responsibe for the formation of trace amounts of 2378-TCDD and 2378-TCDF. To provide EPA with more complete data on the environmental release of these compounds, a new screening study was initiated in April, 1988 to characterize the export from all 104 mills that practice chlorine bleaching of kraft and sulfite produced pulps. This bulletin presents the results of this study and focuses on the distribution of 2378-TCDD/F in bleached pulps, wastewater sludges, and effluents. Since the samples were analyzed at two analytical laboratories, an inter-laboratory comparison study was conducted and is also presented in this bulletin. Similarly, the Agreement with EPA required some limited full congener (PCDDs & PCDFs) analyses in order to further characterize the industry's discharge of CDDs and CDFs. Due to limitations in sample design, the 2378-TCDD/F findings could not be correlated with process control parameters.

KEYWORDS : 2378-TCDD/F, environmental export, screening study, interlaboratory comparison, PCDDs, PCDFs

RELATED NCASI PUBLICATIONS :

(1 ) U.S. Environmental Protection Agency/Paper Industry Cooperative Dioxin Screening Study, NCASI Technical Bulletin No. 545, 1988

(2 ) NCASI Procedures For The Preparation And Isomer-Specific Analysis Of Pulp And Paper Industry Samples For 2378-TCDD and 2378-TCDF, NCASI Technical Bulletin No. 551, 1988

(3 ) A Study Of The Variability Of 2378-TCDD and 2378-TCDF In Bleached Kraft Mill Pulps, Sludges, And Effluents, NCASI Technical Bulletin No. 568, 1989

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# USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY: THE 104 MILL STUDY

## I INTRODUCTION

In March of 1988 the U.S. Environmental Protection Agency (EPA) and the U.S. pulp and paper industry jointly released the results of a screening study (1) that provided some of the first comprehensive results on formation and discharge of chlorinated dibenzodioxins (CDDs) and dibenzofurans (CDFs) in pulp and paper mills. This early screening study of five bleached kraft mills ("Five Mill Study") that used unverified analytical methods confirmed that CDDs and CDFs were formed during the pulp bleaching process. The partitioning of these compounds between the bleached pulp, wastewater treatment sludges, and final effluent was found to be highly variable among the five mills. The study also indicated that 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF) were the principal CDDs and CDFs formed.

To provide the EPA with more complete data on the release of these compounds by the U.S. industry, a new screening study agreement was initiated in April 1988 (Appendix A) to further characterize all 104 U.S. mills that practice chlorine bleaching of kraft or sulfite pulps (2). The five mills who participated in the original study as well as one other mill that independently conducted its own sampling prior to the Agreement were not required to resample. The scope of the study was jointly developed by EPA and industry, and the study was managed by NCASI with EPA overview. The data from this study provide an estimate of the release of 2378-TCDD and 2378-TCDF in three environmental export vectors (bleached pulp, sludge, and effluent) of the U.S. industry as of mid to late 1988.

It is important to point out that the industry initially suggested to EPA that a more comprehensive study be conducted at about 25 bleached mills. The proposed industry study would continue to investigate in a prioritized manner the formation and distribution of 2378-TCDD and 2378-TCDF in the bleach plants and waste water treatment plants. This Intensive Study was ultimately conducted by NCASI with a requirement in the Agreement that the findings be shared with EPA when available. The Intensive Study was designed to investigate possible relationships between TCDD/F formation and bleach plant process operation. This study is in progress and will also be submitted to EPA.

It is also significant to note that many of the analytical issues raised by the industry during the five mill study were not resolved prior to the initiation of this new study of all 104 mills. Consequently, the industry believes that the analytical methods used in this study are methods appropriate for screening studies, but not necessarily valid for regulatory compliance monitoring.

This bulletin will first review the major features of the study design, sample collection, and analytical methodologies. The major findings of the study will then be presented and discussed by export vector. This discussion will focus on a factual presentation of the mass discharge of 2378-TCDD and 2378-TCDF (2378-TCDD/F) and their relative distribution among the three export vectors. Attempts at correlating the mass discharge of 2378-TCDD and 2378-TCDF to bleach plant and/or waste treatment operational parameters are summarized, but not included as major findings of the study. These analyses were limited due to the fact that the study design was developed to document the mass export of PCDD/Fs and not to investigate formation rates as a function of mill/bleach plant configuration and process operations. The latter objective is included in the industry Intensive Study. For the sake of completeness, the data from the 5-Mill Study (and the sixth mill) were included in this bulletin, especially since methodologies were similar in all respects.

## II SCREENING STUDY FEATURES

### A. Study Requirements

The major requirements of the study are outlined below. The timetable for each requirement is detailed in the Agreement(2).

1. Submit companies' previous PCDD/PCDF data to EPA
2. Share NCASI Intensive Study plan and final report when completed
3. Submit schematics of bleach plants and process sewers
4. Submit schematics of wastewater treatment plants
5. Provide narrative on sludge handling and disposal practices
6. Supply "Nominal" bleach plant and wastewater treatment plant operations parameters
7. Submit one year of key waste water treatment plant data
8. Conduct interlaboratory comparison study prior to initiation of sample analyses
9. Submit all analytical data for 2378-TCDD/F on export vectors (with QA/QC data)
10. Submit all analytical data for 35 PCDD/F analyses on export vectors
11. Provide actual bleach plant and waste treatment plant operations data for key parameters during sampling
12. Quarterly updates provided by NCASI on progress in other industry dioxin studies

This bulletin will include a presentation of all analytical data in a mill/company identified form. The process data noted, particularly that from the bleach plant, will be used in the discussion, but mill identification will be omitted. A majority of the mills claimed that some of these data are confidential. They were, however, provided to EPA in order to document the operation of the bleaching and waste treatment processes during sampling.

B. Sample Definitions And Sampling Guidance

The Agreement required that each significant export vector be sampled and the samples composited over a five day period. In most cases the composite samples were comprised of up to eight aliquots per day for a total of 40 aliquots. Nearly all sampling was performed by mill personnel following guidance established by NCASI. EPA reviewed the sampling protocols prior to initiation of the study.

The pulp samples were representative of the highest brightness pulp produced at each bleach line. Hence, at a mill with two bleach lines where hardwood and softwood pulps are bleached, separate hardwood and softwood composite pulp samples were collected. At a mill with a single bleach line where both hardwood and softwood pulps are bleached, sampling was conducted intermittently to insure that the five day composite samples were composed of only hardwood or softwood pulp. For these bleach plants, both species were collected.

Sludge samples consisted of only those sludges removed from the wastewater treatment system and disposed in landfills, incinerated, or disposed of by other methods. Although in most cases the sludges were dewatered prior to offsite disposal, several primary sludges sent to sludge lagoons were collected in a low consistency slurry form.

More than 90 of the effluents sampled were collected from mills with biological treatment followed by secondary settling of suspended solids. The split between activated sludge treatment and aerated basin treatment was about even. For seven additional mills, the samples consisted of partially treated effluents prior to discharge to municipal wastewater treatment plants. For two mills with ocean discharge, untreated effluents were sampled. The sampling frequency for effluents from treatment systems with design residence times greater than 5 days was reduced from 8 aliquots per day to 3 per day.

The industry collected the required samples with its own mill or corporate personnel. NCASI provided both verbal and written instructions and guidance throughout the sample collection phase. For a few mills participating in the NCASI 25 Mill or Intensive Study, NCASI staff assisted with the sampling. A workshop was initially held in May, 1988 to review the Agreement features and to outline the sample collection, preservation, shipping, and chain-of-custody requirements. The key instructions are presented in Appendix B.

## C. Process Information During Sampling

The Agreement required that miscellaneous process information be collected during the sampling period. Included for each stage of the bleach plant were : chemical use, production, Kappa or K Numbers, chlorination stage temperature and pH, and final bleached pulp brightness. The data required from the waste treatment plant were : disharge flow, suspended solids, and sludge production (dry). NCASI prepared the forms displayed in Appendix C to facilitate individual company responses. These data are not presented in any detail in this bulletin due to the business confidential claims made by many of the companies.

# III ANALYTICAL METHODS AND QUALITY CONTROL

## A. General Summary

This sampling scheme generated over 400 samples for isomer-specific 2378-TCDD and 2378-TCDF analyses. About 80 additional samples were collected as part of the quality assurance/quality control plan. These samples were analyzed as field duplicates and/or included in native spike determinations. Samples of each export vector from 9 mills were also analyzed for all 2378-substituted CDDs and CDFs.

All analytical work for this study was conducted by Enseco-California Analytical Laboratories(CAL) in West Sacramento, California, and the Brehm Laboratory at Wright State University (WSU) in Dayton, Ohio. Enseco-CAL performed all of the sludge and effluent analyses, while WSU analyzed most of the pulp samples. NCASI staff performed and coordinated sample preparation, submitting samples to the analytical laboratory, and reviewing laboratory data reports for completeness and accuracy.

## B. Analytical Methods

The analytical methods used by Wright State University for the pulp samples were screening study protocols established during the "Five Mill Study". The effluent and sludge sample methods used by Enseco-CAL are reported in NCASI Technical Bulletin No. 551 (4). Analytical target detection limits for 2378-TCDD and 2378-TCDF were 1 ng/kg(ppt) for sludges and pulps, and 0.01 pg/l (ppq) for wastewater effluents. The detection limits achieved in the analyses ranged from 0.1 ng/kg to 0.6 ng/kg (ppt) for pulps, 0.3 ng/kg to 3.0 ng/kg for wastewater sludges, and from 0.003 pg/l to 0.017 pg/l (ppq) for wastewater effluents. All results for pulps and sludges are reported on a dry weight basis.

C. Quality Assurance/Control Objectives

The QA/QC objectives of this study were defined in Attachment 6 of the Agreement(2). These criteria for identification and quantitation of 2378-TCDD and 2378-TCDF were as follows:

| 2378-TCDD | | 2378-TCDF | |
|---|---|---|---|
| Ion Ratio 320/322 | 0.65 - 0.89 | Ion Ratio 304/306 | 0.65 - 0.89 |
| % Recovery Internal Standard | 40 - 120 % | % Recovery Internal Standard | 40 - 120 % |

If an analytical result did not meet the QA/QC criteria described in Attachment 6, NCASI reviewed the analytical data received from the contract laboratory to determine what corrective steps were appropriate. More specifically, if internal standard recoveries were below 20%, the analyses were repeated with a portion of the original 5 day composite sample. If, after two analyses, the internal standard recoveries were still under 20%, both of the analyses were reported as PEQ (present, estimated quantitation) when the analyte was positively identified or PND (probably not detected) with the estimated detection limit in parentheses. The respective ion ratio and internal standard recovery for each analysis were also reported.

The QA/QC samples in this study consisted of laboratory and field duplicates along with replicate samples spiked with known concentrations of 2378-TCDD/F. The QA/QC objective was 20 % of all samples submitted for each of the three matrices.

During the course of the study, approximately 25 % of the effluents and fewer than 10 % of the pulps and sludges failed either of the quality assurance criteria stated. In most cases, these problems were resolved following a single reanalysis. Six of the problematic effluent samples were not resolved following the required reanalysis. For these samples, several companies elected to either resample or provide alternative 2378-TCDD/F data. For one effluent sample four analyses were conducted without satisfying the QA/QC criteria.

D. Interlaboratory Comparison Studies

Because more than one contract laboratory was used to analyze for 2378-TCDD/F, an interlaboratory comparison study was conducted prior to any routine submittal of samples. As noted previously, the sludge and effluent samples were analyzed by Enseco-CAL while the pulp samples were analyzed by Wright State University. Pulp samples collected from those mills participating in the NCASI Intensive Study ("25 Mill Study") were also analyzed by Enseco-CAL.

The results of these analyses are noted in Table 1.

These data clearly indicate the potential for significant differences between laboratories for all three sample types, especially wastewater effluents. Note for the effluent samples ILC-2 and ILC-6 that the results are not-detected for one laboratory but detected for the other two. Similar examples were observed for the pulps (ILC-2 and ILC-5) and sludge (ILC-5). These differences are to some extent mitigated in screening studies by choosing one laboratory to analyze all samples of the same matrix. Screening studies provide estimates of gross amounts of 2378-TCDD/F present and relative differences between mills. These laboratory differences, however, are critical for regulatory permit compliance purposes where the absolute quantity must be known.

Table 1 Results Of 104 Mill Study Interlaboratory Comparison

| | LABORATORY 2378-TCDD (ng/kg, ppt) | | | LABORATORY 2378-TCDF (ng/kg, ppt) | | |
|---|---|---|---|---|---|---|
| PULP: | A | B | C | A | B | C |
| ILC-1 | 8.4 | 6.8 | ND(6) | 50 | 51 | 51 |
| ILC-2 | 3.9 | 3.1 | 3.3 | 7.2 | 5.3 | ND(5.2) |
| ILC-3 | 7.3 | 6.5 | 13 | 9.6 | 7.5 | 11 |
| ILC-4 | 6.0 | 4.1 | 3.4 | 68 | 48 | 34 |
| ILC-5 | 0.9 | ND(0.2) | ND(0.3) | 9.5 | 1.4 | ND(0.8) |
| ILC-6 | 14 | 9.4 | 13 | 69 | 75 | 89 |
| ILC-7 | 2.2 | 1.9 | 2.4 | 6.9 | 5.7 | 6.5 |
| SLUDGE: | 2378-TCDD (ng/kg, ppt) | | | 2378-TCDF (ng/kg, ppt) | | |
| | A | B | C | A | B | C |
| ILC-1 | 140 | 140 | 134 | 1500 | 2240 | 2261 |
| ILC-2 | 30 | 30 | 29 | 150 | 182 | 147 |
| ILC-3 | 52 | 49 | 50 | 68 | 72 | 66 |
| ILC-4 | 24 | 21 | 19 | 160 | 204 | 173 |
| ILC-5 | ND(4.5) | 13 | 9.1 | 47 | 69 | 46 |
| ILC-6 | 160 | 160 | 153 | 440 | 897 | 769 |
| ILC-7 | 13 | 12 | 17 | 42 | 50 | 42 |
| EFFLUENT: | 2378-TCDD (pg/l, ppq) | | | 2378-TCDF (pg/l, ppq) | | |
| | A | B | C | A | B | C |
| ILC-1 | 150 | 110 | 117 | 1400 | 2200 | 1906 |
| ILC-2 | 44 | ND(21) | 29 | 88 | 88 | 81 |
| ILC-3 | ND(17) | ND(3) | ND(32) | 39 | 7 | 7.6 |
| ILC-4 | 100 | 86 | - | 980 | 939 | - |
| ILC-5 | ND(8.5) | ND(3) | ND(6.3) | 44 | ND(1) | ND(8.5) |
| ILC-6 | 44 | ND(5) | 44 | 190 | 225 | 225 |
| ILC-7 | ND(17) | ND(8) | ND(11) | 40 | 23 | 27 |

## IV BLEACH PLANT AND WASTE TREATMENT PLANT OPERATIONS

### A. Overview Of Bleaching Practices

At the time of sampling in mid-1988, the distribution of bleaching lines based upon wood species and chlorine and chlorine dioxide use was as described in Table 2.

Furthermore, oxygen delignification systems had been installed on seven bleach lines at the time of the study. Presently, many companies are making numerous bleaching changes, some of which include increasing capability for chlorine dioxide substitution, improved brownstock washing, and oxygen delignification systems. Chlorine dioxide substitution was generally low with about 1/3 of the mills having none at the time of sampling. Any overall characterization of industry bleaching practices described in this bulletin is now considered out-of-date due to the many changes underway.

Note that in several cases the mills claimed the bleach plant process data confidential and did not provide it to NCASI but did supply it to EPA. Two mills at the time of sampling were only using hypochlorite and were not included in Table 2.

Table 2 General Distribution Of Pulping And Bleaching Practices Employed in 104 Mill Study - 1988-89

| | Number of Bleach Lines | | | | | | |
|---|---|---|---|---|---|---|---|
| | Chlorine Use | | | $ClO_2$ Substitution | | | |
| Wood Species | 1-3 % | 3-5 % | >5 % | 0 % | 1-10 % | 11-40 % | >40 % |
| Hardwood | 28 | 39 | 6 | 24 | 22 | 24 | 3 |
| Softwood | 5 | 27 | 57 | 43 | 30 | 14 | 2 |
| Mixed | 0 | 5 | 5 | 6 | 2 | 2 | 0 |

### B. Overview Of Waste Treatment Practices

The general waste treatment practices are summarized in Table 3. They are categorized as activated sludge, aerated basin, and municipal treatment systems (POTWs). Most mills were discharging treated effluent into a receiving stream at the time of sampling. Several mills temporarily diverted effluents to holding basins due to discharge license requirements that restricted discharge during low flow, high temperature summer conditions. The most common sludge disposal practice was landfilling. Several mills, however, either incinerated sludge or landspread sludge during selected periods of the year. A few mills did not mechanically dewater primary sludges and stored the residuals in sludge lagoons onsite.

## V. DISTRIBUTIONS OF 2378-TCDD/F IN EXPORT VECTORS

All analytical data for 2378-TCDD/F are summarized in Appendix D by mill code and state. This summary also includes the type of pulping - kraft or sulfite. Appendix F summarizes additional data on pulps, sludges, and effluents collected and analyzed by the industry since completion of the sampling for this study. These more recent data, included for the sake of completeness, illustrate the major reductions in 2378-TCDD/F export since completion of the 104 Mill Study.

### A. Distributions For Final Bleached Pulps

1. General Summary - In this section the concentrations of 2378-TCDD and 2378-TCDF for both bleached kraft and sulfite pulps are summarized. Data from the 5-Mill Study are also included. The summaries will show hardwood and softwood bleached pulps separately. For purposes of this bulletin, analyses for 2378-TCDD/F that were reported as non-detect will be assumed to be 0 ng/kg (ppt). These data are shown for both bleached kraft and sulfite pulps in Table 4 and graphically in Figures 1 and 2. In the table, the results are displayed overall and by geographic region -northern, pacific northwest, and southern. The average, minimum, and maximum values are shown along with the number of non-detect analyses. Several bleach lines represented in the overall summary do not appear in the more specific regional or specie summaries because they bleached mixed species or species not reported to NCASI.

Table 3 General Distribution Of Waste Treatment Practices Employed During 104 Mill Study

| Aerated Stabilization Treatment | Number Of Facilities |
|---|---|
| Northern Mills | 14 |
| Southern Mills | 39 |
| **Activated Sludge Treatment** | |
| Northern Mills | 30 |
| Southern Mills | 11 |
| **Primary Only/POTW** | |
| All Mills | 11 |

Note : Some mills in the study had more than one discharge

2. <u>Significance Of Bleached Pulp Findings</u> - The data presented in <u>Table 4</u> suggest that the average 2378-TCDD/F concentrations for hardwood pulps are less than those for softwood pulps from the same geographic region. These differences were most pronounced for both the northern and northwest regions. Furthermore, the average 2378-TCDD/F concentrations for southern kraft softwood pulps were apparently lower than those from corresponding softwood pulps in all northern regions.

The average concentration for all sulfite pulps is less than that for all kraft pulps. When kraft and sulfite mill pulps are compared on the basis of similar wood species, the average concentrations are more similar. It is important to point out, however, that a greater portion of sulfite pulp analyses were reported as non-detected than for any group of kraft pulps.

<u>Table 4</u> 2378-TCDD/F Concentrations For Bleached Kraft Pulps 1988 - 89

| Geographic Region | Number Pulps | Average (ng/kg) (ppt) | Minimum (ng/kg) (ppt) | Maximum (ng/kg) (ppt) | Number Of Non-Detect |
|---|---|---|---|---|---|
| | | (2378-TCDD / 2378- TCDF) | | | |
| ALL BLEACHED PULPS | 180 | 8/89 | ND/ND | 116/2620 | 32/10 |
| BLEACHED KRAFT PULPS | | | | | |
| Northern Hardwood | 17 | 5/44 | ND/1 | 17/180 | 2/0 |
| Northern Softwood | 11 | 25/253 | 2/7 | 116/1110 | 0/0 |
| Northwest Hardwood | 3 | 4/11 | ND/1 | 8/20 | 1/0 |
| Northwest Softwood | 17 | 17/342 | 2/3 | 56/2620 | 0/0 |
| Southern Hardwood | 45 | 5/55 | ND/ND | 33/661 | 8/2 |
| Southern Softwood | 55 | 8/48 | ND/ND | 43/632 | 6/3 |
| BLEACHED SULFITE PULPS | | | | | |
| Northern Hardwood | 8 | 4/46 | ND/ND | 15/223 | 5/2 |
| Northwest Softwood | 8 | 0.4/53 | ND/ND | 3/409 | 7/2 |

<u>In considering the implications of these findings, it is important that readers be aware that the pulps in any of the arbitrary categories presented in Table 4 represent a wide range of bleach plant operating practices and a wide array of end product uses of the bleached pulps, requiring different pulp properties.</u>

The pulp samples were collected following the final stage of pulp washing in each bleach plant. For many mills, the pulp undergoes additional washing and refining prior to the manufacture of a variety of paper grades or drying prior to sale as market pulp. These processes have the potential to further reduce the 2378-TCDD/F concentrations in bleached pulps. In the 5 Mill Study(1), for example, the maximum concentrations of 2378-TCDD/F in paper machine whitewaters were 0.10 pg/l(ppq) and 0.35 pg/l (ppq), respectively. This observation could become important in the evaluation of total mill export for some mills.

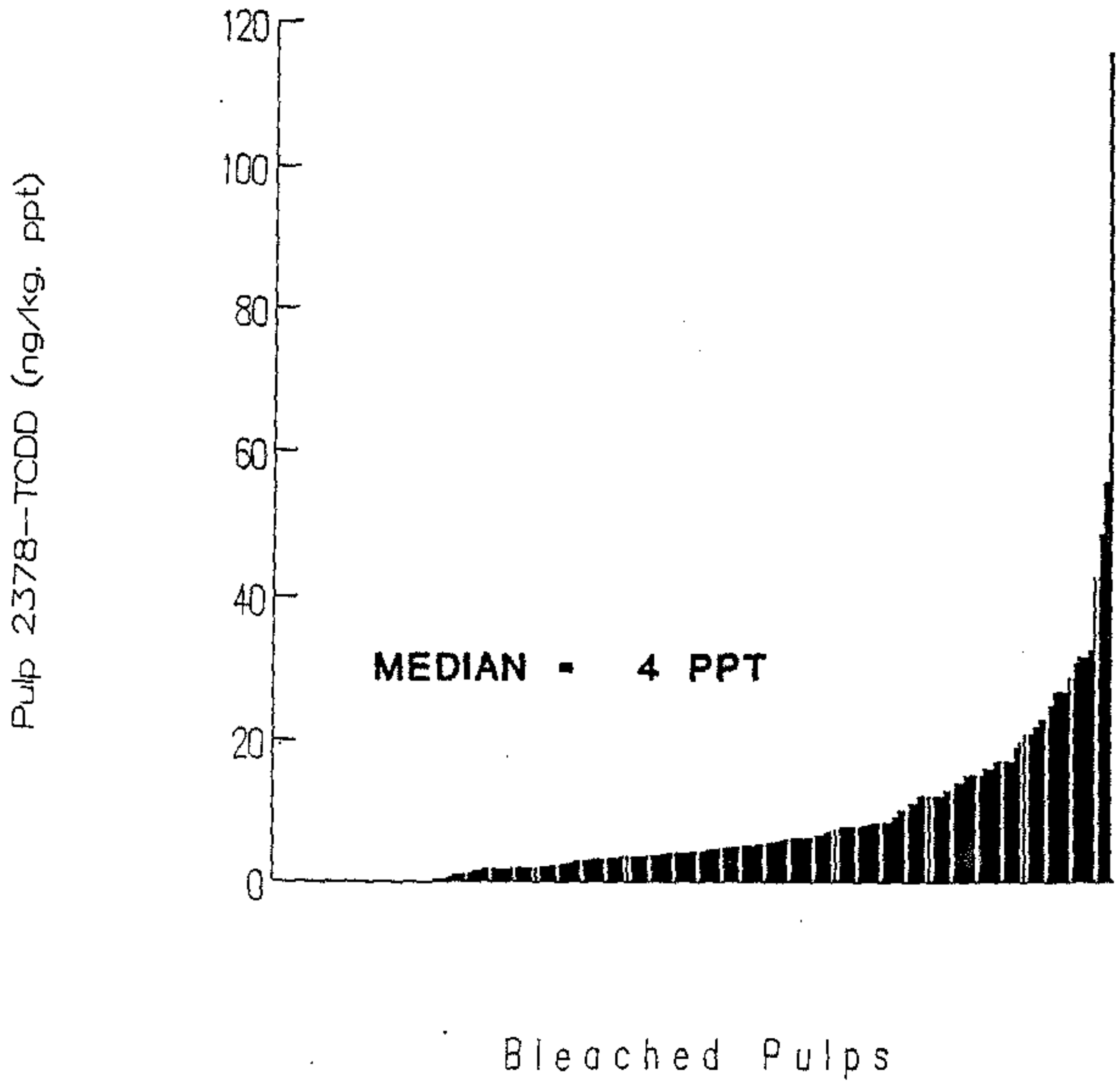



FIGURE 1 DISTRIBUTION OF BLEACHED PULP 2378-TCDD CONCENTRATIONS FOR 104 MILL STUDY - 1988-89

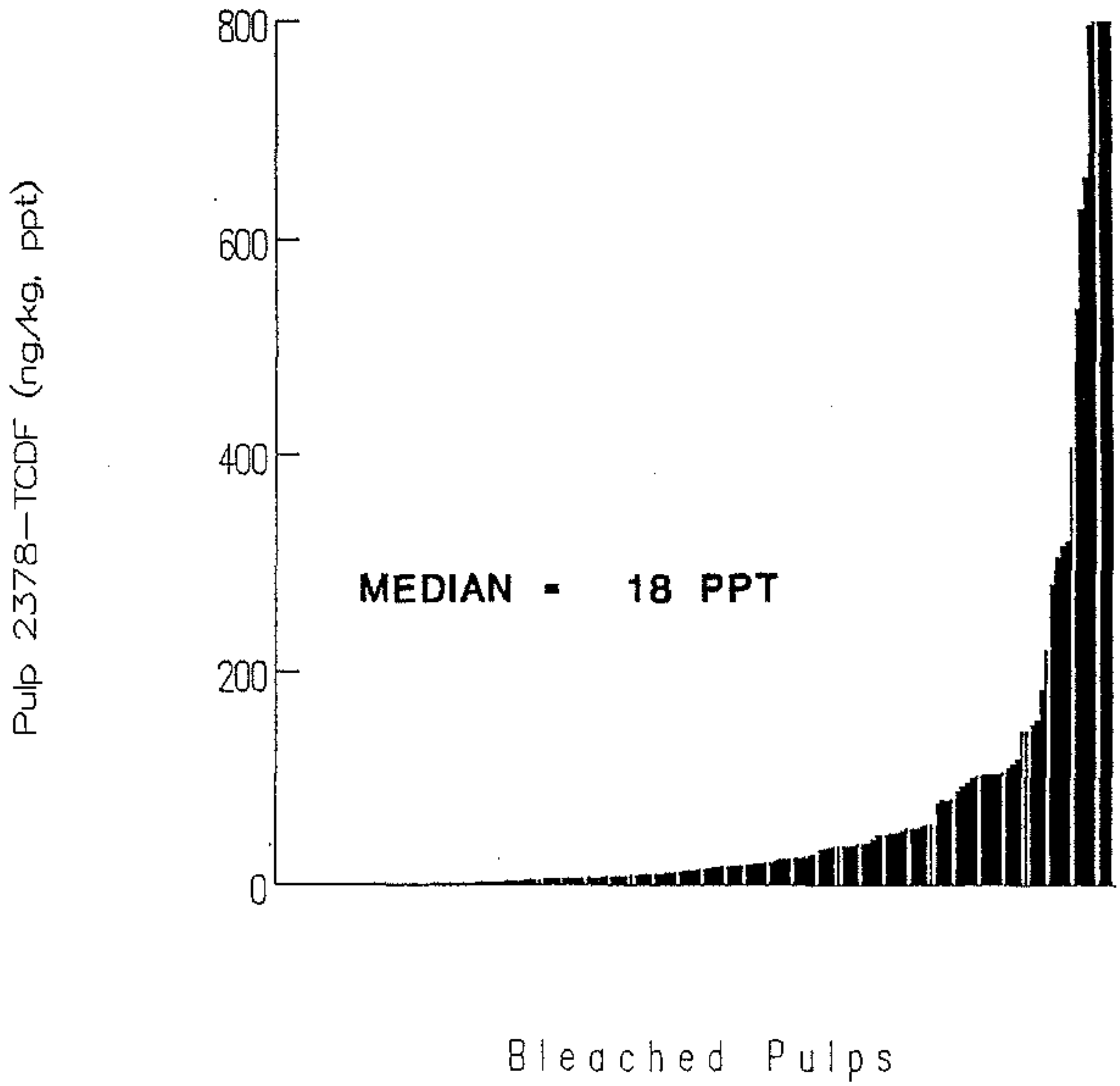



FIGURE 2 DISTRIBUTION OF BLEACHED PULP 2378-TCDF CONCENTRATIONS FOR 104 MILL STUDY - 1988-89

Although all pulp samples were collected and composited over a 5-day period to reduce the potential impact of process variability, there was no assurance that miscellaneous process variability in either bleach plant chemical use and/or operation did not affect the 5-day average concentrations of 2378-TCDD/F. Data from the NCASI Variability Study (3), suggested that significant trends in bleach pulp TCDD/F content over time were possible in spite of the apparent steady state in bleach plant chemical use and operational factors(production rate, K Number, temperature, pH).

Readers are again advised that the 2378-TCDD/F found in the bleached pulp does not represent all that was formed. The sampling program did not directly account for any 2378-TCDD/F in bleach plant filtrates. Any TCDD/F in these streams was ultimately captured in either the wastewater treatment plant sludges or effluent. For this major reason, no attempts were made to correlate the TCDD/F findings in pulps with bleach plant operating parameters. Although the total mill export was probably a reasonable estimation of that generated in the bleach plant(s) for those mills with activated sludge treatment, most of the mills had multiple bleaching lines. It was simply not possible to isolate that portion of the total mill TCDD/F export assosciated with any given bleach line.

<u>3. Bleached Pulp Quality Assurance/Quality Control Results</u> - In addition to the results reported in the previous section, 48 analyses were conducted for quality control purposes. These samples included field and/or laboratory duplicate pairs as well as samples spiked with known amounts of 2378-TCDD/F. The results of the duplicate analyses are shown in <u>Table 5</u>, while the native spike determinations and recovery calculations are summarized in <u>Table 6</u>. There were 27 paired analyses; two were non-detect for 2378-TCDD, and one was non-detect for 2378-TCDF. The Relative Percent Difference (RPD) statistic was used to characterize the results from these paired analyses. It is defined as the (Range/Average) x 100%. The median RPD for the 2378-TCDD data was 8% with a range from 0% to 84%. The corresponding median RPD for the 2378-TCDF data was also 8% with a range of 0% to 67%. It is significant to note that the duplicate paired samples that produced RPD statistics greater than 50 % were field duplicates and not lab duplicates.

All twenty-one native spike determinations summarized in <u>Table 6</u> were within the 50% to 150% range specified by the QA/QC objectives of the Agreement. In general, the data shown in both <u>Tables 5</u> and <u>6</u> indicate that in most cases the pulp analyses were reliable and reproducible by the contract laboratory.

Table 5 Bleached Pulp Duplicate Analyses For 2378-TCDD/F

| 2378-TCDD (ng/kg, ppt) Rep 1 | Rep2 | RPD[1] (%) | 2378-TCDF (ng/kg, ppt) Rep 1 | Rep 2 | RPD[1] (%) |
|---|---|---|---|---|---|
| ND* | ND* | na | AD** | 6.4 | na |
| ND* | 6.3 | na | 0.90 | 1.1 | 20.0 |
| 1.7 | 1.6 | 6.1 | 1.0 | 1.4 | 33.3 |
| 1.9 | 1.6 | 17.1 | 1.3 | 1.5 | 14.3 |
| 2.0 | 4.9 | 84.1 | 2.8 | 2.8 | 0.0 |
| 3.2 | 3.3 | 3.1 | 3.5 | 2.9 | 18.8 |
| 3.6 | 6.0 | 50.0 | 5.8 | 6.9 | 19.0 |
| 3.9 | 3.8 | 2.6 | 8.0 | 9.4 | 16.1 |
| 4.2 | 4.4 | 4.7 | 11 | 5.5 | 66.7 |
| 4.4 | 4.7 | 6.6 | 12 | 17 | 34.6 |
| 5.1 | 5.7 | 11.1 | 12 | 11 | 8.7 |
| 5.2 | 5.4 | 3.8 | 22 | 23 | 4.4 |
| 6.3 | 6.1 | 3.2 | 28 | 26 | 7.4 |
| 6.5 | 4.6 | 34.2 | 37 | 35 | 5.6 |
| 7.7 | 7.8 | 1.3 | 38 | 41 | 7.6 |
| 8.5 | 7.9 | 7.3 | 48 | 66 | 31.6 |
| 9.2 | 10 | 8.3 | 50 | 45 | 10.5 |
| 11 | 9.1 | 18.9 | 55 | 52 | 5.6 |
| 12 | 11 | 8.7 | 55 | 54 | 1.8 |
| 14 | 18 | 25.0 | 68 | 39 | 54.2 |
| 15 | 15 | 0.0 | 74 | 74 | 0.0 |
| 16 | 17 | 6.1 | 83 | 79 | 4.9 |
| 17 | 16 | 6.1 | 97 | 98 | 1.0 |
| 18 | 15 | 18.2 | 103 | 108 | 4.7 |
| 20 | 18 | 10.5 | 104 | 71 | 37.7 |
| 21 | 23 | 9.1 | 153 | 147 | 4.0 |
| 25 | 27 | 7.7 | 647 | 661 | 2.1 |

* Analyte not detected ** Analytical difficulties

[1] RPD = Relative Percent Difference (Range/Average)x100%

Table 6 Bleached Pulp Native Spike Recoveries Of 2378-TCDD/F

| Analyte | Number Of Spikes | % Recovery Of Spike Range |
|---|---|---|
| 2378-TCDD | 21 | 90 % - 138 % |
| 2378-TCDF | 21 | 69 % - 100 % |

## B. Distributions For Wastewater Sludges

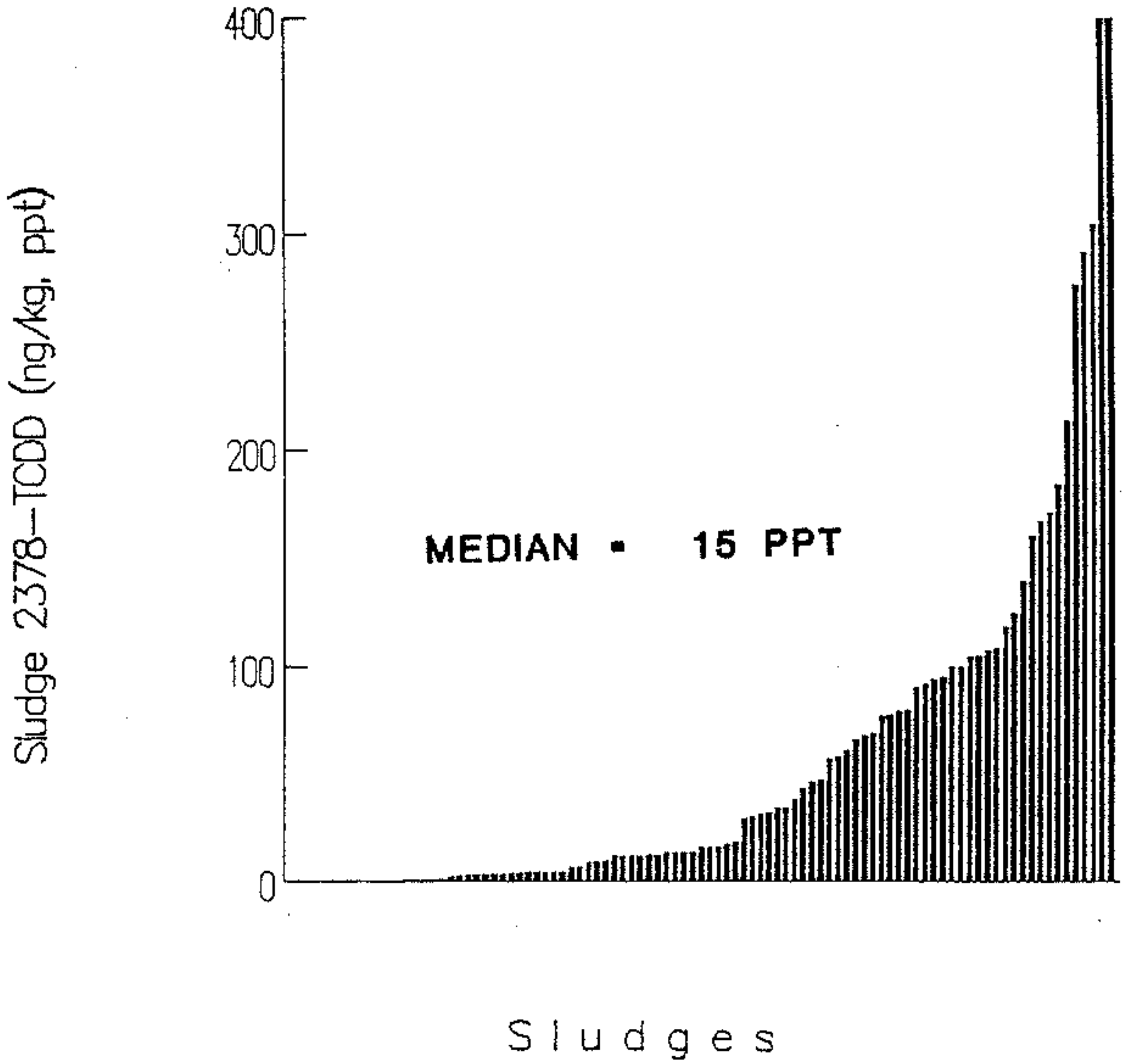
1. General Summary - In this section, the concentrations of 2378-TCDD and 2378-TCDF for wastewater treatment plant sludges are summarized. The summary will include combined sludges from mills with activated sludge systems, and primary sludges from mills with aerated stabilization basins. Comparisons based upon wood species were not possible because most of the mills had more than one bleaching line using different wood species. Hence, concentrations in the effluent could not be directly related to any one bleaching line due to the sampling limitations.

The data are shown in Table 7 and graphically in Figures 3 and 4. The data in Table 7 are further delineated by pulping process and geographic region. The average, minimum, and maximum values are shown along with the number of non-detect analyses. In this bulletin, analyses that were reported as non-detect were assumed to equal 0 ng/kg (ppt) for purposes of averaging.

Most of the sludges analyzed were either primary sludges from aerated basin treatment systems or combined primary and secondary sludges from activated sludge systems. In a few cases, the sludges were collected as a slurry from a sludge disposal lagoon. The study design did not provide for an opportunity to compare the 2378-TCDD and 2378-TCDF concentrations in primary only versus secondary only sludges.

Table 7 2378-TCDD/F Concentrations For Wastewater Sludges 1988-89

| | Number Sludges | Average (ng/kg) (ppt) | Minimum (ng/kg) (ppt) | Maximum (ng/kg) (ppt) | Number Of Non-Detect |
|---|---|---|---|---|---|
| ALL MILLS | | | | | |
| Combined Sludges | 41 | 73/381 | ND | 756/2550 | 1/0 |
| Primary Sludges | 58 | 64/679 | ND | 1390/17100 | 1/0 |
| Secondary Sludges | 6 | 226/2332 | 7/29 | 710/10900 | 0/0 |
| ALL SULFITE MILLS | | | | | |
| Combined Sludges | 10 | 14/51 | ND | 58/150 | 1/0 |
| Primary Sludges | 5 | 17/206 | 5/32 | 35/584 | 0/0 |
| ALL NORTHERN KRAFT MILLS | | | | | |
| Combined Sludges | 12 | 81/681 | 5/55 | 180/2550 | 0/0 |
| Primary Sludges | 7 | 22/130 | ND/7 | 67/380 | 1/0 |
| All NORTHWEST KRAFT MILLS | | | | | |
| Combined Sludges | 5 | 55/474 | 30/89 | 101/1570 | 0/0 |
| Primary Sludges | 7 | 69/1300 | 0.06/0.2 | 278/6740 | 0/0 |
| ALL SOUTHERN KRAFT MILLS | | | | | |
| Combined Sludges | 13 | 123/351 | 3/2 | 756/1300 | 0/0 |
| Primary Sludges | 38 | 79/744 | 0.05/0.2 | 1390/17100 | 0/0 |




<u>FIGURE 3</u> <u>DISTRIBUTION OF SLUDGE 2378-TCDD CONCENTRATIONS FOR 104 MILL STUDY - 1988-89</u>

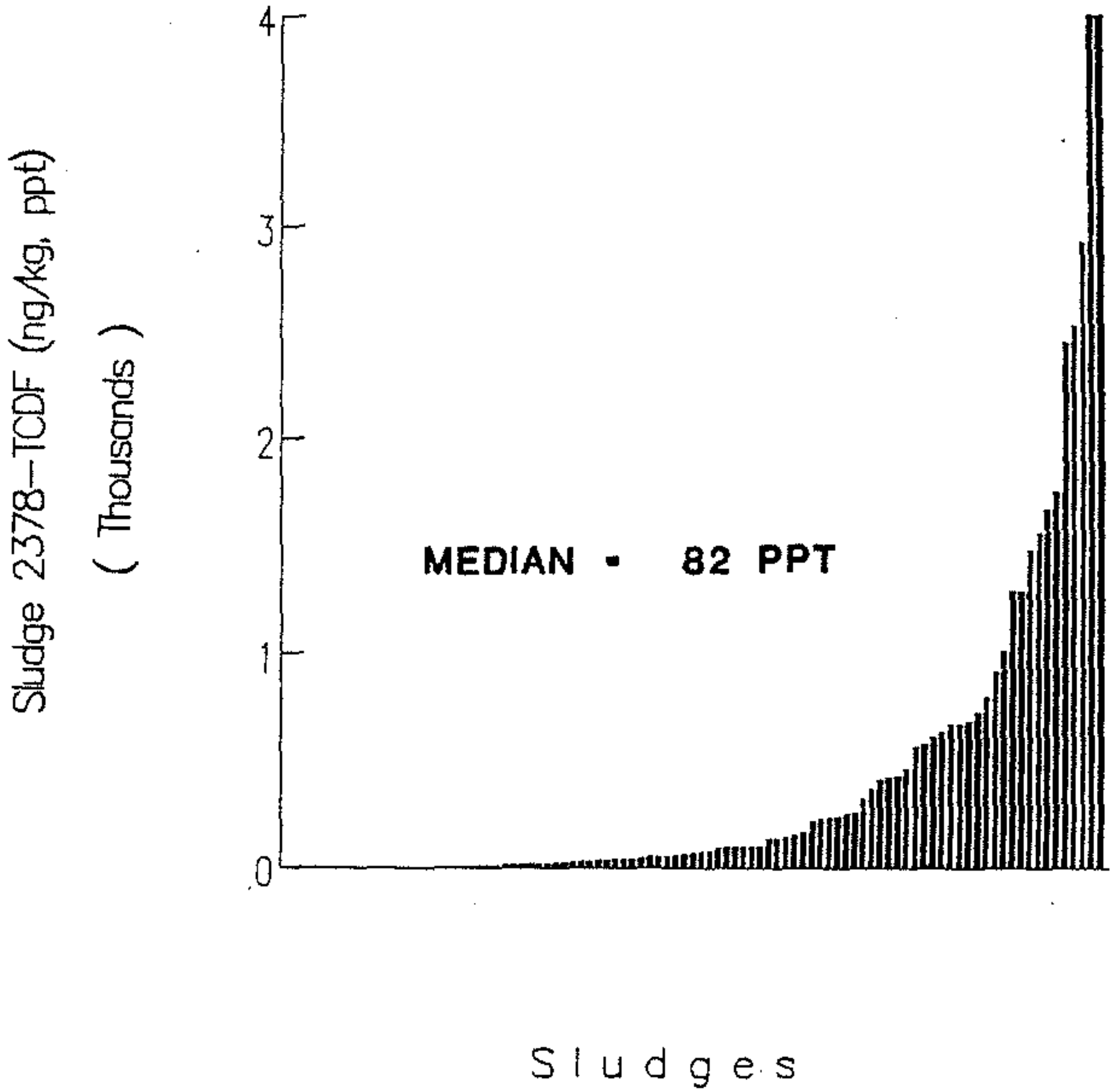



FIGURE 4 DISTRIBUTION OF SLUDGE 2378-TCDF CONCENTRATIONS FOR 104 MILL STUDY - 1988-89

2. Significance Of Wastewater Sludge Findings - The average concentrations of 2378-TCDD for all kraft primary sludges was about 12 % lower than that for kraft combined sludges. More significant differences between primary and combined sludges were noted in both the northern and southern kraft groupings. In these cases, the average primary sludge concentrations were less than the combined sludges. Although not conclusive, this observation suggests that the 2378-TCDD concentration in secondary sludge is generally higher than primary sludges. This observation was noted originally for the six secondary sludges from the Five Mill Study, but it could not be verified in this study due to the lack of a sufficient number of secondary sludge measurements. Also, a different analytical laboratory was used for samples in the Five Mill Study than was used in this study.

The only clear differences in the groupings shown in Table 7 are (a) southern kraft mill combined sludges as a group had higher 2378-TCDD/F concentrations than all other categories, and (b) sulfite mill sludges(combined only and primary only) had lower concentrations than the corresponding kraft mill only groupings. It is also significant to note that there were only 3 non-detect 2378-TCDD/F concentrations in sludges in the entire study population. Due to the vast differences in sludge age and treatment plant operations, the significance of these findings and observations is unclear. This study was not designed to explicitly investigate these factors.

The 2378-TCDD/F concentrations reported for primary sludges that were significantly less than 1 ng/kg (ppt) were for non-dewatered sludge slurries with consistencies generally less than 1%. These samples were analyzed as liquids but reported as a sludge in this study.

The NCASI variability study (3) observed that the 2378-TCDD/F content of both primary and combined sludges were variable over time. The combined effects of analytical, sampling, and process variability were in the range of 20% to 40%. This observed variability, however, could not be correlated to treatment plant or mill manufacturing process operations. Further attempts at correlating the sludge data from this study with treatment plant process conditions was not valid.

3. Wastewater Sludge Quality Assurance/Quality Control Results - In addition to the results reported in the previous section, 31 analyses were conducted for quality control purposes. These samples included field and/or laboratory duplicate pairs as well as samples spiked with known amounts of 2378-TCDD/F. The results of the duplicate analyses are shown in Table 8, while the native spike determinations and recovery calculations are summarized in Table 9. There were 14 paired analyses; two included analytical difficulties for 2378-TCDD, and one analytical difficulty for 2378-

TCDF. The Relative Percent Difference (RPD) statistic was used to characterize the results from these paired analyses. It is defined as the (Range/Average) x 100 %. The median RPD for the 2378-TCDD data was 17% with a range from 0% to 55%. The corresponding median RPD for the 2378-TCDF data was 17% with a range of 3.5% to 50%. It is significant to note that the duplicate paired samples that produced RPD statistics greater than 50 % were field duplicates and not lab duplicates.

All except one of the seventeen native spike determinations for 2378-TCDD/F summarized in Table 9 were within the 50% to 150% range specified by the QA/QC objectives of the Agreement. In general, the data shown in both Tables 8 and 9 indicate that in most cases the sludge analyses were reliable and reproducible by the contract laboratory.

The 2378-TCDD/F concentrations reported for primary sludges that were less than 1 ng/kg (ppt) were for non-dewatered sludge slurries with consistencies generally less than 1%. These samples were analyzed as liquids and treated essentially like an effluent sample in this study.

The combined effects of analytical, sampling, and process variability were estimated by NCASI to be in the range of 20% to 40% for sludges(3). This observed variability, however, could not be correlated to treatment plant or mill operations. Further attempts at correlating the sludge data from this study with treatment plant process conditions was not valid.

Table 8 Wastewater Sludge Duplicate Analyses For 2378-TCDD/F

| 2378-TCDD (ng/kg, ppt) | | | 2378-TCDF (ng/kg, ppt) | | |
|---|---|---|---|---|---|
| Rep 1 | Rep 2 | RPD[1] | Rep 1 | Rep 2 | RPD[1] |
| 3.8 | 2.9 | 26.9 | AD** | 260 | na |
| 4.1 | 3.2 | 24.7 | 5.2 | 3.3 | 44.7 |
| 11 | 9.4 | 15.7 | 56 | 68 | 19.4 |
| 18 | 18 | 0.0 | 73 | 90 | 20.9 |
| 25 | AD** | na | 80 | 84 | 4.9 |
| 28 | 35 | 33.3 | 80 | 89 | 10.7 |
| 33 | 39 | 16.7 | 101 | 106 | 4.8 |
| 39 | 29 | 29.4 | 106 | 149 | 33.7 |
| 71 | AD** | na | 147 | 169 | 13.9 |
| 81 | 73 | 10.4 | 373 | 393 | 5.2 |
| 81 | 68 | 17.4 | 373 | 342 | 8.7 |
| 175 | 172 | 1.7 | 615 | 637 | 3.5 |
| 198 | 176 | 11.8 | 1000 | 600 | 50.0 |
| 373 | 213 | 54.6 | 1920 | 1600 | 18.2 |

** Analytical Difficulties

[1]RPD = Relative Percent Difference (Range/Average)x100%

Table 9 Wastewater Sludge Native Spike Recoveries Of 2378-TCDD/F

| Analyte | Number Of Spikes | % Recovery Of Spike Range |
|---|---|---|
| 2378-TCDD | 17 | 76 % - 150 % |
| 2378-TCDF | 17 | 54 % - 156 %* |

* Outside of QA/QC range of 50 % - 150 %

## C. Distributions For Wastewater Effluents

1. General Summary - In this section the 2378-TCDD/F concentrations for wastewaters are summarized. The summary will show the results based upon pulping process, geographic region, and wastewater treatment type. Any comparisons based upon wood species was not possible because most of the mills employed more than one bleaching line with different wood species. Hence, concentrations in the effluent could not directly related to any one bleaching line due to the sampling limitations.

The data are shown in Table 10 and graphically in Figures 5 and 6. The summary in Table 10 further delineates the data by pulping process and geographic region. The average, minimum, and maximum values are shown along with the number of non-detect analyses. For purposes of this bulletin, analyses that were reported as non-detect were assumed to equal 0 pg/l (ppq).

2. Significance Of Wastewater 2378-TCDD/F Findings - The data in Table 10 suggest that those mills using activated sludge treatment discharge somewhat smaller amounts of 2378-TCDD/F than those with aerated basins. This observation is apparent for the grouping that includes all mills as well as the northwest kraft mills, but not for the northern and southern kraft groupings or for sulfite mills. Analyses from activated sludge systems also had a higher frequency of non-detect concentrations when compared with aerated basin systems. In general the sulfite mill effluents had lower concentrations of 2378-TCDD/F and a higher frequency of non-detects when compared to all other mill categories.

In reviewing these data for wastewater effluents, readers are advised to consider the results of the NCASI variability study(3). This variability study provided data on both analytical and process variability for activated sludge and aerated basin treatment systems. The most significant finding from this study was that analytical variability, characterized by a coefficient of variation, was about 56%. The high analytical component of the total variability was attributed to inconsistent laboratory performance that led to poor precision between batches. Given the low effluent concentrations (pg/l,ppq) in many of the industry's treated effluents and the current level of method development and lack of rigorous validation, this result was not unexpected.

Table 10 2378-TCDD/F Concentrations For Wastewaters 1988-89

| | Number Of Effluents | Average (pg/l ) (ppq) | Minimum (pg/l ) (ppq) | Maximum (pg/l ) (ppq) | Number Of Non-Detect |
|---|---|---|---|---|---|
| ALL EFFLUENTS | | | | | |
| Aerated Basin | 51 | 72/673 | ND/ND | 640/8400 | 8/4 |
| Activated Sludge | 41 | 36/215 | ND/ND | 250/2200 | 14/4 |
| Primary/None | 14 | 22/124 | ND/3 | 100/660 | 3/0 |
| ALL NORTHERN KRAFT MILLS | | | | | |
| Aerated Basin | 5 | 12/50 | ND/14 | 41/94 | 2/0 |
| Activated Sludge | 13 | 42/408 | ND/12 | 120/2200 | 2/0 |
| ALL NORTHWEST KRAFT MILLS | | | | | |
| Aerated Basin | 6 | 125/2767 | 3/ND | 360/8400 | 0/1 |
| Activated Sludge | 5 | 18/223 | ND/37 | 49/800 | 1/0 |
| ALL SOUTHERN KRAFT MILLS | | | | | |
| Aerated Basin | 36 | 79/448 | ND/ND | 640/4000 | 5/3 |
| Activated Sludge | 11 | 69/206 | ND/ND | 250/730 | 3/1 |
| ALL SULFITE MILLS | | | | | |
| All Treatment | 15 | 6/95 | ND/ND | 23/840 | 9/3 |
| Aerated Basin | 3 | 6/425 | ND/35 | 10/840 | 1/0 |
| Activated Sludge | 12 | 6/12 | ND/ND | 23/36 | 8/3 |
| ALL NO TREATMENT/PRIMARY ONLY/POTW | | | | | |
| All Mills | 14 | 22/124 | ND/3 | 100/660 | 3/0 |

The NCASI variability study also evaluated effluent process variability for two mills: one with an activated sludge treatment system, and the other with an aerated basin system with about 10 days retention in treatment. The data from the aerated basin system, based upon weekly samples collected for 10 weeks, suggested an element of process related variability that was greater than that attributable to analytical variabilty. In the case of the activated sludge system, based upon daily samples collected for 10 days, no conclusion regarding process variability could be made because the analytical variability estimate was greater than the apparent process variability observed.

These results suggest that the effluent analyses obtained in the 104 Mill Study are significantly limited by analytical variability concerns that at this point are not well understood or characterized. For this reason, the differences observed between treatment system type are probably not significant and no summary statistics are provided. Long term process variability that could occur over a period of several months is not well characterized.

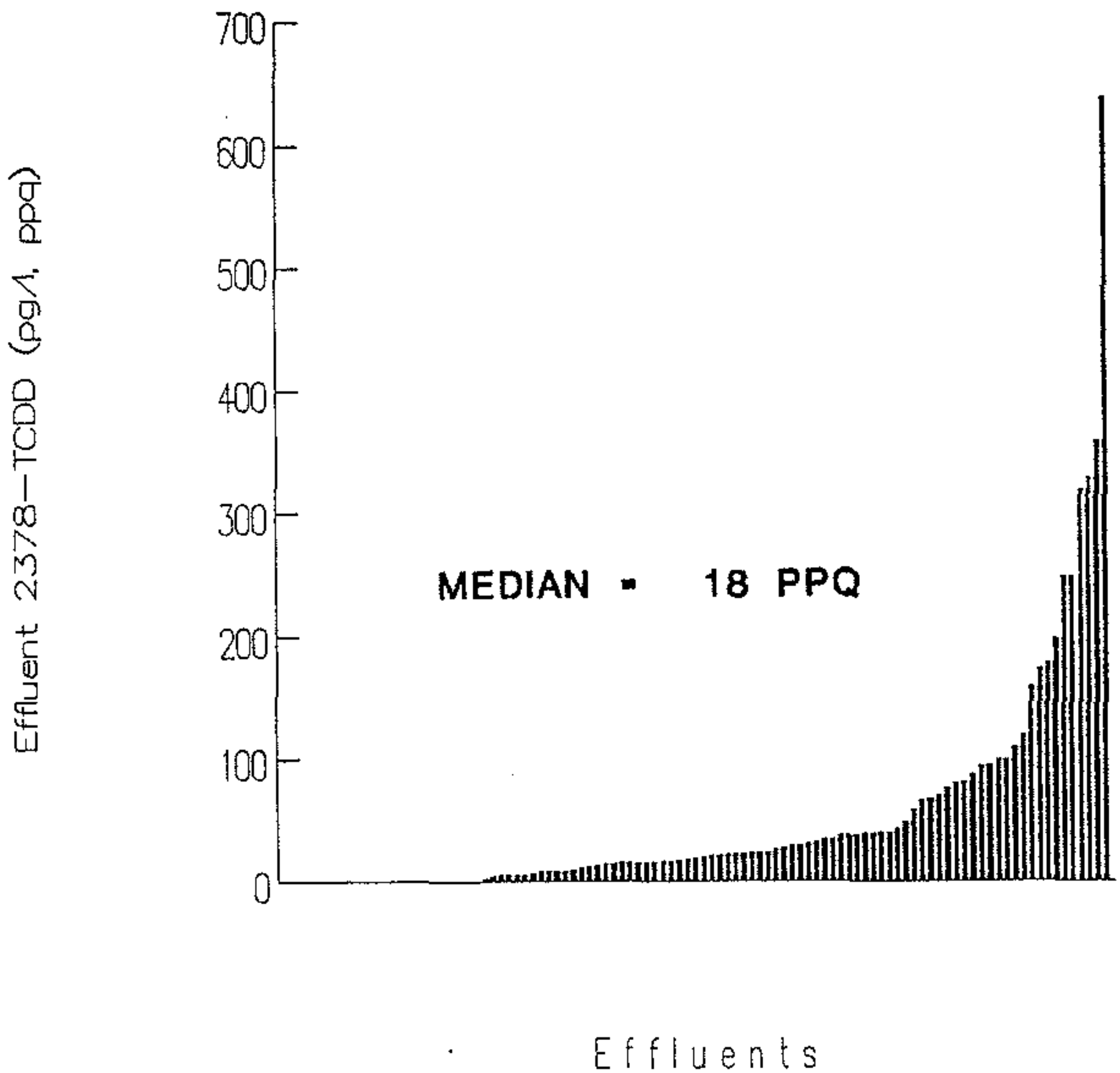



FIGURE 5 DISTRIBUTION OF EFFLUENT 2378-TCDD CONCENTRATIONS FOR 104 MILL STUDY - 1988-89

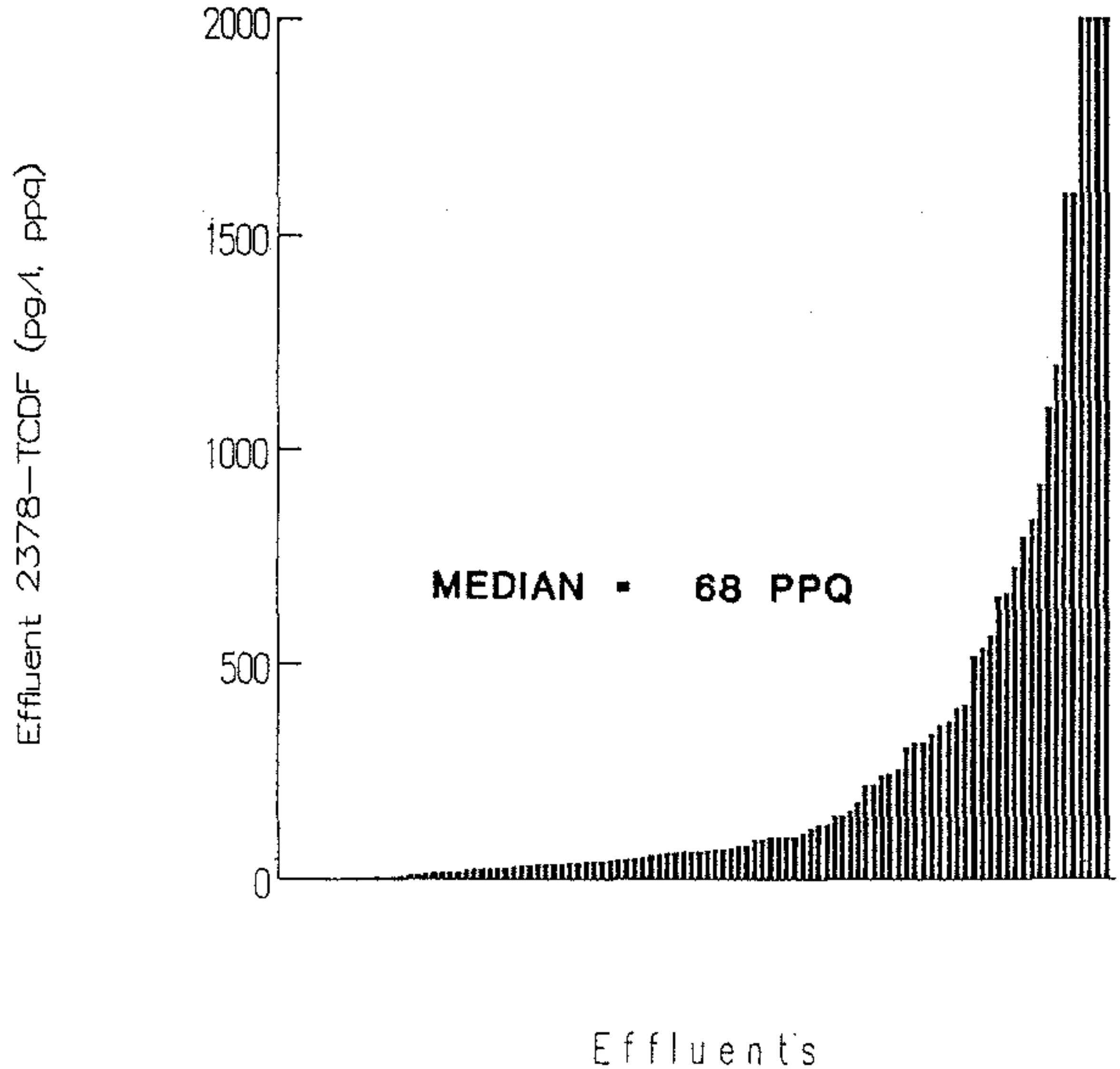



FIGURE 6 DISTRIBUTION OF EFFLUENT 2378-TCDF CONCENTRATIONS FOR 104 MILL STUDY - 1988-89

The Five Mill Study results suggested that there could be a relationship between effluent 2378-TCDD/F and its suspended solids content. This hypothesis is based upon the fact that dioxins and furans have low solubilities in water and will preferentially partition to solid phases with high organic carbon contents. A general correlation of the 2378-TCDD content with suspended solids is shown in Figure 7. Although the overall trend is poor, there are several points that need to be considered. First, the analytical variability for 2378-TCDD in the effluent is large and could account for a large part of the variance shown in Figure 7. Secondly, the Five Mill Study, as well as the data from this study, indicate that factors which affect partitioning between pulp, sludge, and wastewaters are not known and are highly variable between mills. The correlation attempted in Figure 7 should be based upon mills that are similar with respect to bleach plant generation rates, waste treatment facilities and performance, and partitioning between solid and aqueous phases. Unfortunately there was insufficient data in the study to evaluate this correlation further. As was the case with the bleached pulp data, the study was not designed to properly evaluate process cause and effect relationships in the waste treatment systems. Consequently, no conclusion with respect to TCDD/F correlation with suspended solids could be made.

3. Wastewater Effluent Quality Assurance/Quality Control Results - In addition to the results reported in the previous section, 30 analyses were conducted for quality control purposes. These samples included field and/or laboratory duplicate pairs as well as samples spiked with known amounts of 2378-TCDD/F. The results of the duplicate analyses are shown in Table 11, while the native spike determinations and recovery calulations are summarized in Table 12. There were 14 paired analyses; two included analytical difficulties for 2378-TCDD, and one analytical difficulty for 2378-TCDF. The Relative Percent Difference (RPD) statistic was used to characterize the results from these paired analyses. It is defined as the (Range/Average) x 100 %. The median RPD for the 2378-TCDD data was 16% with a range from 0% to 32%. The corresponding median RPD for the 2378-TCDF data was 15% with a range of 0% to 55%. It is significant to note that the duplicate paired samples that produced RPD statistics greater than 50 % were field duplicates and not lab duplicates.

All except one of the sixteen native spike determinations for 2378-TCDD/F summarized in Table 12 were within the 50% to 150% range specified by the QA/QC objectives of the Agreement.

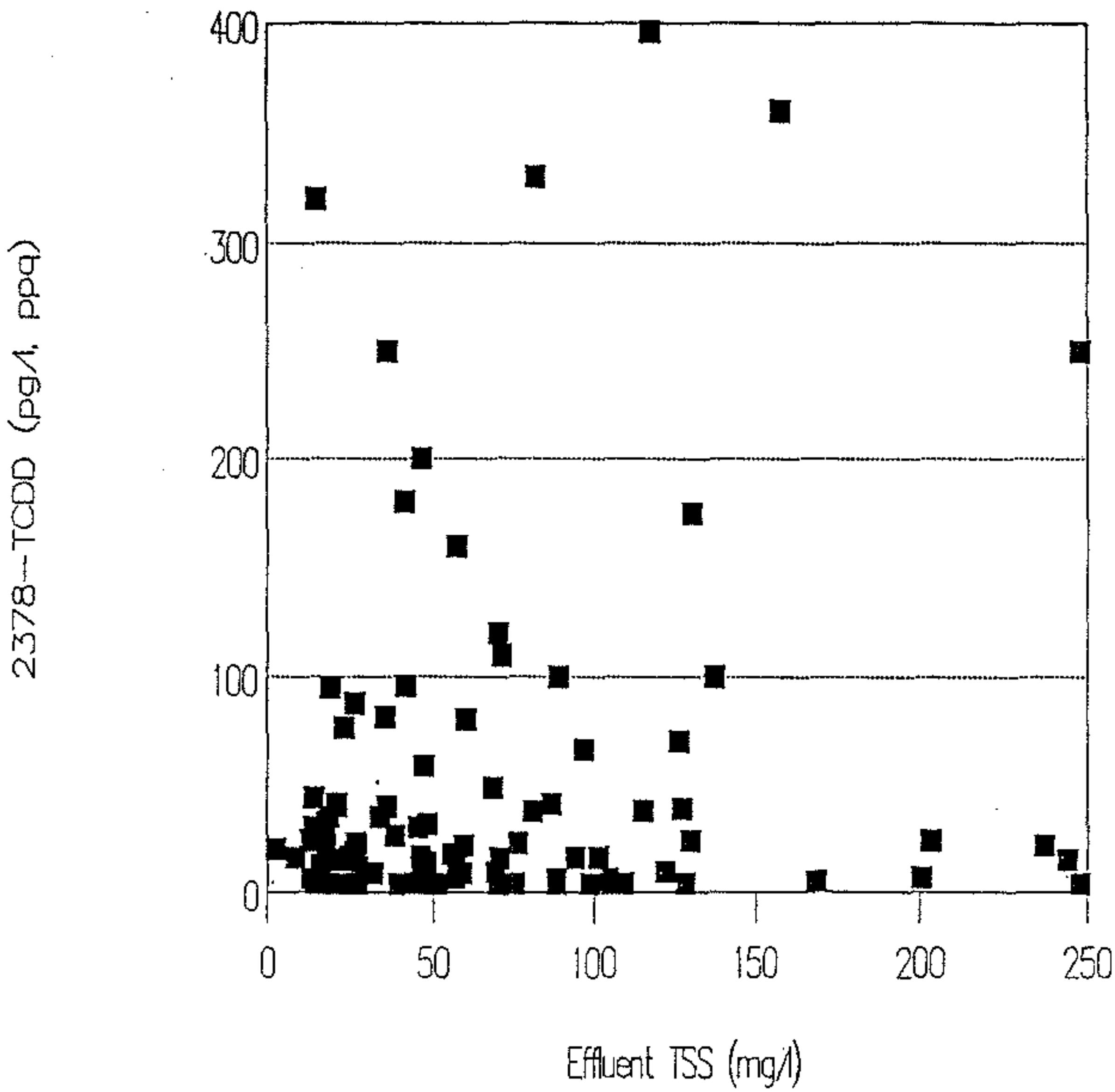



FIGURE 7 EFFLUENT 2378-TCDD CONCENTRATION VS SUSPENDED SOLIDS CONCENTRATIONS FOR 104 MILL STUDY

Table 11 Summary Of Wastewater Effluent Duplicate Analyses For 2378-TCDD/F

| 2378-TCDD (pg/l, ppq) | | | 2378-TCDF (pg/l, ppq) | | |
|---|---|---|---|---|---|
| Rep 1 | Rep 2 | RPD[1] | Rep 1 | Rep 2 | RPD[1] |
| AD** | AD** | na | AD** | AD** | na |
| AD** | AD** | na | 18 | 24 | 28.6 |
| 10 | 8.5 | 16.2 | 26 | 22 | 16.7 |
| 12 | 12 | 0.0 | 37 | 21 | 55.2 |
| 13 | 18 | 32.3 | 43 | 44 | 2.3 |
| 18 | 24 | 28.6 | 68 | 50 | 30.5 |
| 19 | 16 | 17.1 | 72 | 54 | 28.6 |
| 19 | 15 | 23.5 | 100 | 63 | 45.4 |
| 30 | 30 | 0.0 | 150 | 160 | 6.5 |
| 41 | 40 | 2.5 | 190 | 190 | 0.0 |
| 44 | 32 | 31.6 | 250 | 250 | 0.0 |
| 71 | 79 | 10.7 | 360 | 320 | 11.8 |
| 95 | 120 | 23.3 | 540 | 630 | 15.4 |
| 490 | 640 | 26.5 | 1500 | 1600 | 6.5 |

** Analytical difficulties

[1] RPD = Relative Percent Difference (Range/Average)x100%

Table 12 Summary Of Wastewater Effluent Native Spike Recoveries Of 2378-TCDD/F

| Analyte | Number Of Spikes | % Recovery Of Spike Range |
|---|---|---|
| 2378-TCDD | 16 | 72 % - 132 % |
| 2378-TCDF | 16 | 47 % - 140 % |

## VI. TOTAL MILL EXPORT OF 2378-TCDD/F

### A. Mass Flows of 2378-TCDD/F

Estimated mass flows of 2378-TCDD/F total mill exports from kraft and sulfite mill categories are summarized in Table 13. These results are presented in terms of lbs/ton of air-dried brownstock pulp (ADBSP) include data from only those mills with complete mass flow data for pulp, sludge, and effluent and complete analytical data for 2378-TCDD/F. There were a few mills where significant analytical difficulties prevented a fair assessment of the total mill export of either 2378-TCDD or 2378-TCDF. In these cases, NCASI elected to exclude these mills from the summary table that follows. For purposes of this bulletin, analyses that were reported as non-detect were assumed to equal 0 ng/kg (ppt) in the export vector calculations.

There were also a few mills that did not provide bleach plant production data to NCASI, but did provide it to EPA with claims of confidentiality. Therefore, NCASI elected to remove this data from the discussion of total mill export. Also, two mills in the study were soda mills and were excluded from both the kraft and sulfite mill categories.

Note that calculated total mill mass flow rates for mills with aerated stabilization basins may not fully reflect the rates of formation of 2378-TCDD/F. The results for those mills are probably biased low due to some retention of 2378-TCDD/F in sludge in aerated lagoons which would not have been fully characterized by the sampling program. Accordingly, the results presented are believed to be representative of total mill exports for all mills at the time of sampling, but not necessarily fully representative of the total amount of 2378-TCDD/F formed. <u>Based upon the preliminary study results, the amounts of 2378-TCDD and 2378-TCDF formed at all 104 mills on an annual basis are estimated to be in the range of 1.6 lbs (0.73 kg) and 12.2 lbs (5.5 kg), respectively</u>. These quantities are estimated to be less than 3 % of the total generated in the U.S. each year(6).

On an industry-wide average mass basis, the amount of 2378-TCDD in the three export vectors was distributed uniformly for 2378-TCDD: pulp 40%, effluent 30%, and sludge 30%. The distribution for 2378-TCDF was slightly different: pulp 50%, effluent 30%, and sludge 20%. However, as was noted in the Five Mill Study, the distributions of 2378-TCDD/F among pulp, effluent, and sludge were highly variable from mill to mill. There were mills in the study where all of the 2378-TCDD/F formed was found in either the pulp, sludge, or effluent vector with none in the other two vectors. No general conclusions regarding distribution in export vectors could be reached for any of the various mill production or geographic categories.

There was only one mill in the study that was non-detected for 2378-TCDD in all export vectors. This mill utilized a conventional bleaching sequence, discharged directly into a municipal treatment system, and produced no sludge on-site. It is also important to note that many of the mills with low 2378-TCDD/F export were also practicing conventional pulping and bleaching; in other words, without the use of oxygen delignification and/or high levels of chlorine dioxide substitution. The mills in the latter category were low in 2378-TCDD/F export compared to the average for all mills. <u>Low 2378-TCDD/F export, however, was not limited to mills with oxygen delignification and/or high chlorine dioxide substitution</u>.

Table 13 Distribution of Total Mill Exports of 2378-TCDD/F Based For 104 Mill Study - 1988-89

(Results in 10-7 lbs/ton ADBSP)

| | Number of Mills | Average | Minimum | Maximum |
|---|---|---|---|---|
| ALL MILLS | 97* | | | |
| 2378-TCDD | | 0.4 | 0.0 | 3.0 |
| 2378-TCDF | | 4.4 | 0.7 | 95.4 |
| | Yearly Total = | 1.6 lb 2378-TCDD / year | | |
| | = | 12.2 lb 2378-TCDF / year | | |
| ALL KRAFT MILLS | 82 | | | |
| 2378-TCDD | | 0.5 | 0.0 | 3.0 |
| 2378-TCDF | | 4.8 | 0.007 | 95.4 |
| | Yearly Total = | 1.5 lb 2378-TCDD / year | | |
| | = | 11.4 lb 2378-TCDF / year | | |
| ALL SULFITE MILLS | 13 | | | |
| 2378-TCDD | | 0.2 | 0.007 | 0.7 |
| 2378-TCDF | | 2.6 | 0.001 | 12.7 |
| | Yearly Total = | 0.1 lb 2378-TCDD / year | | |
| | = | 0.7 lb 2378-TCDF / year | | |

Note: (1) Results for mills with complete analytical and mass flow data included. Mass flows are affected by sludge retention in aerated stabilization basins. (2) ADBSP - Air-Dried Brownstock Pulp. (3) Two soda mills included only in "ALL MILLS" category.

## B. Mill Operations and Formation of 2378-TCDD/F

Preliminary analyses of the formation of 2378-TCDD/F with respect to bleach plant chemical application rates and operating parameters were attempted but not found to be useful since the sampling program was not designed to collect all the necessary bleach plant samples . Figure 8 is a plot of 2378-TCDD formed, as characterized by export vector measurements, vs active chlorine applied in C-stages for all kraft mills. While the data indicate a general trend of increasing 2378-TCDD with increasing chlorine application, there is no direct correlation evident when all mills are considered together. A similar plot for 2378-TCDF is shown in Figure 9. The distribution of results suggest that, for certain mills, factors other than chlorine application appear to have a more significant impact on formation of 2378-TCDF than on formation of 2378-TCDD.

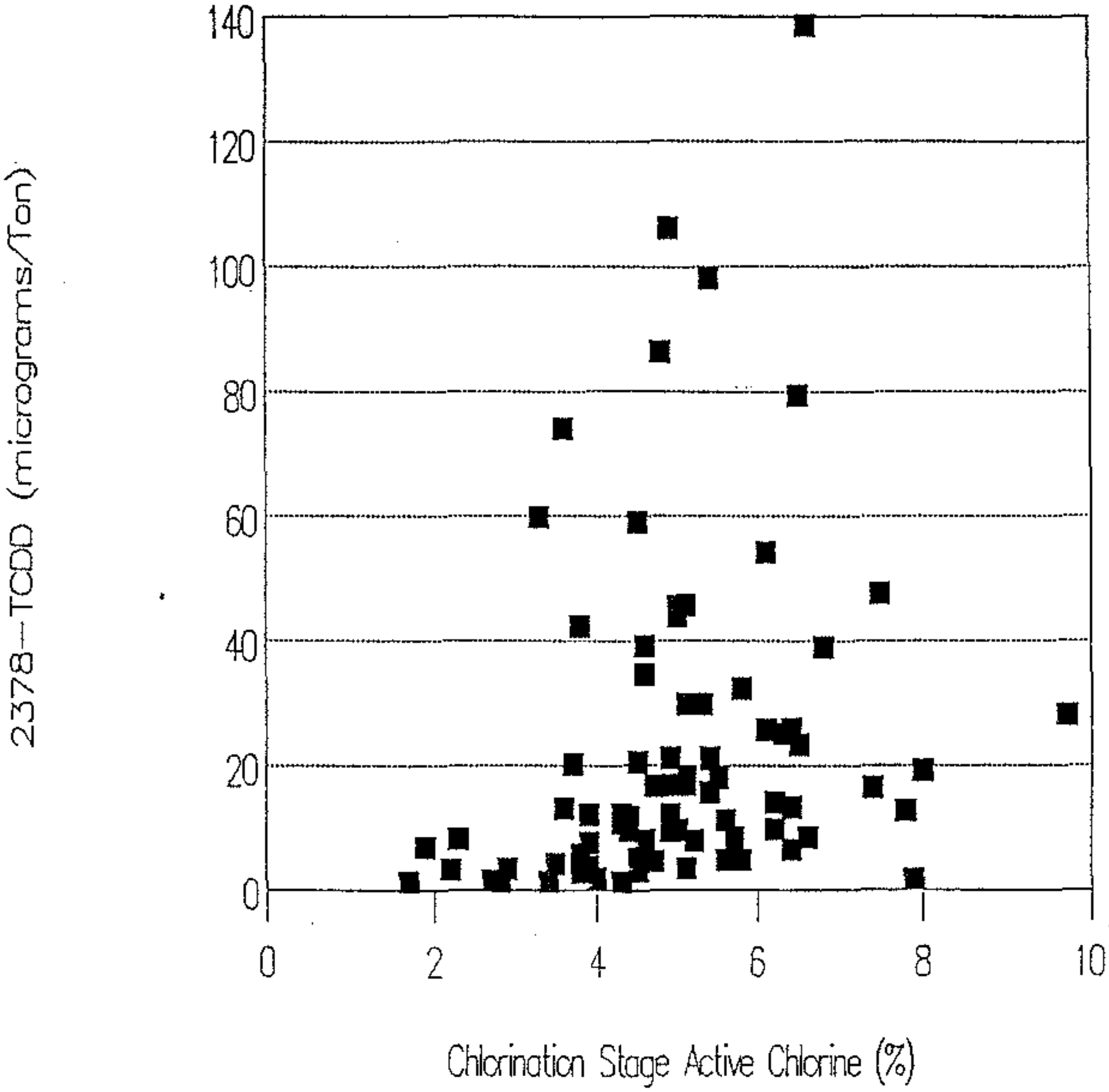



FIGURE 8 104 MILL STUDY (1988-89) TOTAL MILL EXPORT OF 2378-TCDD VS CHLORINATION STAGE TOTAL ACTIVE CHLORINE USE

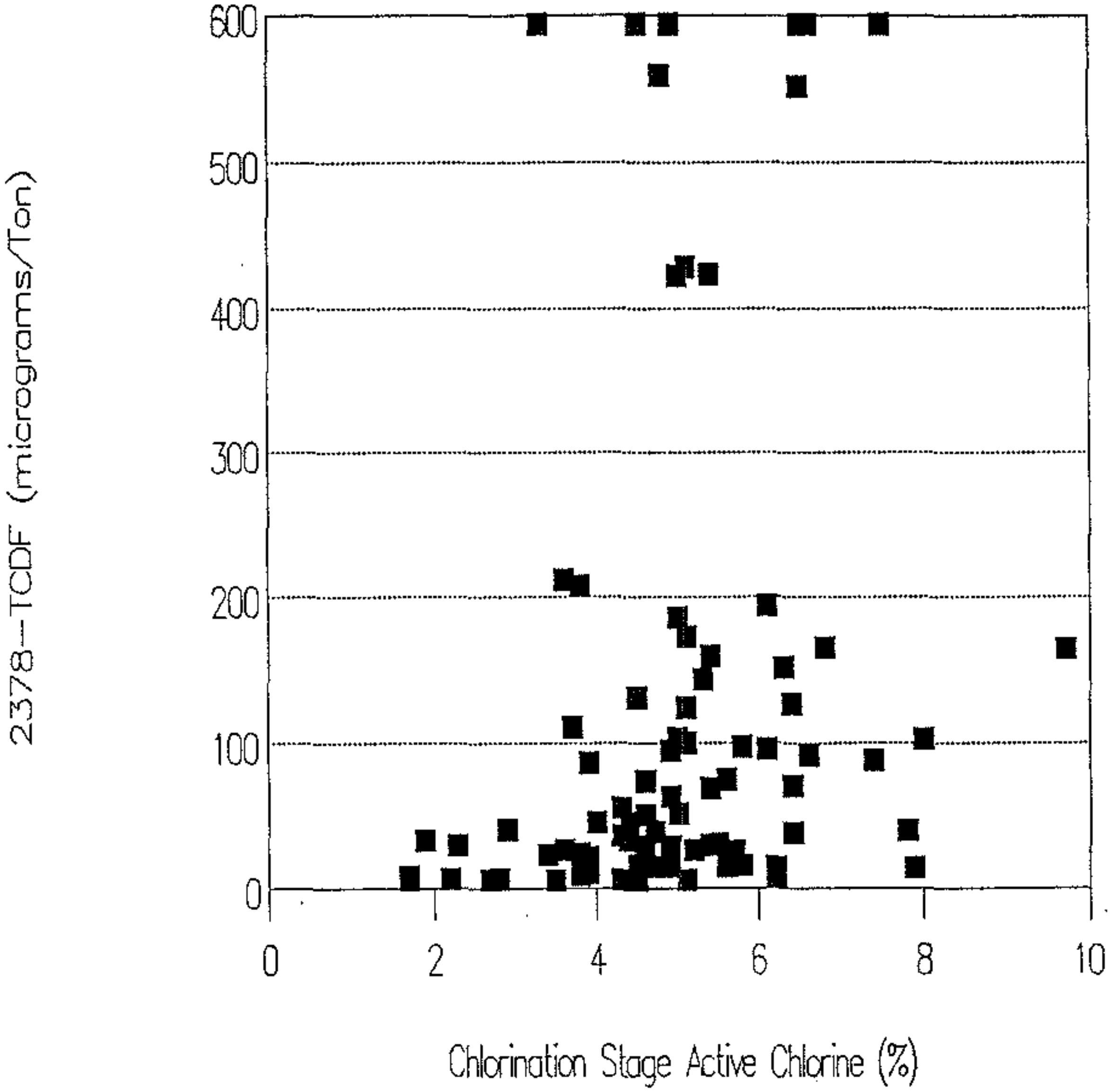



FIGURE 9 104 MILL STUDY (1988-89) TOTAL MILL EXPORT OF 2378-TCDF VS CHLORINATION STAGE TOTAL ACTIVE CHLORINE USE

## VII FULL CONGENER ANALYSES

The Agreement required that 35 samples be submitted for full congener analyses. The pulps, sludges, and treated effluents from nine mills were submitted to a single laboratory for these analyses. The target analytes included eleven substituted PCDDs and 14 PCDFs. The results are summarized in Tables 14 to 16 for pulps, sludges, and effluents, respectively. A more detailed summary of all of these results, including the QA/QC duplicates and native spike determinations are presented in Appendix E. In addition to the measured concentrations, 'Toxicity Equivalents'(TEQ) are calculated using the 1989 International TEFs(5). These data demonstrate that the 2378-TCDD/F congeners represent the more significant portion of the calculated toxicity.

These results indicate that 2378-TCDD and 2378-TCDF represent 93% to 100% of the toxicity equivalence. In a few cases where the 2378-TCDD and 2378-TCDF concentrations were very low (one sludge and several effluents), the TEQ due to 2378-substituted isomers was found to be less than 90% of the total TEQ.

## VII PRELIMINARY FINDINGS AND CONCLUSIONS

1. A screening study of 2378-TCDD/F export from all 104 mills in the U.S. practicing chlorine bleaching was sucessfully completed. Data from the study provide a rough estimate of the 2378-TCDD/F export from all 104 mills as of mid-1988 through early 1989. Due to the limitations in analytical methods alone, the data are not considered appropriate for use in regulatory permit situations.

2. The amounts of 2378-TCDD and 2378-TCDF formed in the U.S. bleached kraft industry in mid to late 1988 were estimated to be 1.6 lbs/yr (0.7 kg/yr) and 12.2 lbs/yr (5.5 kg/yr), respectively. These results are further estimated to be less than 3 % of the total generated in the U.S. each year.

3. Partitioning of 2378-TCDD/F export among pulp, sludge and wastewater effluent was highly variable from mill to mill, but the overall distribution was about 40%, 30%, and 30%, respectively.

4. An interlaboratory comparison study on each export vector was conducted that highlighted significant differences between laboratories for some pulp, sludge, and effluents samples. The differences were more significant for the effluent samples than for pulps and sludges. In some cases, one laboratory reported a non-detect when the other laboratories reported dectects. In order to mitigate the effect of these differences, all wastewater sludge and effluent samples were processed at one laboratory and all pulps at another.

5. The study relied upon two contract laboratories using analytical methods appropriate for screening study objectives. The methods are described in the Five Mill Study report for bleached pulp samples, and in NCASI Technical Bulletin No. 551 for wastewater sludges and

effluents. Target analytical detection limits of 1 ng/kg (ppt) for pulps and sludges, and 10 pg/l (ppq) for effluents were achieved for nearly all samples.

6. Bleached softwood kraft pulps generally had higher concentrations of 2378-TCDD/F than bleached hardwood pulps. Similarly, bleached kraft pulps generally had higher concentrations than bleached sulfite pulps.

7. Bleached kraft mills had higher concentrations of 2378-TCDD/F in wastewater effluents and sludges than sulfite mills.

8. The effluent concentration of 2378-TCDD/F in mills utilizing activated sludge treatment was somewhat less than that for mills with aerated basin treatment. Because of known analytical limitations, these differences were not considered conclusive by NCASI.

9. The export of 2378-TCDD/F could not be related to bleach plant and waste treatment process operations due to limitations in the study design. No reliable statistical relationships were found, for example, between bleach plant operating parameters such as chlorine use and the export of 2378-TCDD/F. Similarly, there was no relationship between effluent and sludge 2378-TCDD/F export and waste treatment operations, including the suspended solids content of the treated wastewater.

10. Full congener analyses on 35 samples indicated that the 2378-TCDD/F components generally represented 97 % to 100 % of the toxicity equivalence for bleached pulp, sludge, and wastewater effluents.

## IX LITERATURE REFERENCES

(1) U. S. EPA/Paper Industry Cooperative Dioxin Screening Study, Office of Water, Office of Water Regulations and Standards, Washington, DC, EPA-440/1-88-025.

(2) U. S. EPA- Paper Industry Cooperative Screening Study Agreement, April 25, 1988, Washington, DC.

(3) "A Study Of The Variability Of 2378-TCDD And 2378-TCDF In Bleached Kraft Mill Pulps, Sludges, and Treated Effluents," NCASI Technical Bulletin No. 568, New York, NY 10016 (1989)

(4) "NCASI Procedures For The Preparation And Isomer-Specific Analysis Of Pulp And Paper Industry Samples For 2378-TCDD and 2378-TCDF," NCASI Technical Bulletin No. 551, New York, NY, 10016 (1989)

(5) Interim Procedures For Estimating Risks With Exposure To Mixtures Of CDDs and CDFs And 1989 Update (I-TEFs/89), EPA/625/3-89/016 (1989)

(6) NCASI Corporate Correspondence CC - 89-80, June 28, 1989, 260 Madison Avenue, New York, NY

Table 14 104 Mill Study Pulp Full Congener Analyses 1988-89

| Analyte | Mill A | Mill B | Mill C | Mill C (Replicate) | Mill D |
|---|---|---|---|---|---|
| | | ( ng/kg, ppt ) | | | |
| 2378-TCDD | 21 | 5.9 | 1.7 | 0.4 | 6.8 |
| non-2378-TCDD | 1.1 | ND(0.3)a | ND(0.3)a | ND(0.3)a | ND(0.5)a |
| 12378-PeCDD | 1.4 | ND(0.3) | ND(0.4) | ND(0.1) | ND(0.1) |
| non-2378-PeCDD | 1.1 | 0.3 | ND(0.4) | ND(0.1) | ND(0.1) |
| 123478-HxCDD | ND(0.6) | ND(0.2) | ND(0.5) | ND(0.2) | ND(0.6) |
| 123678-HxCDD | ND(0.6) | ND(0.2) | ND(0.5) | ND(0.2) | ND(0.6) |
| 123789-HxCDD | ND(0.6) | ND(0.2) | ND(0.5) | ND(0.2) | ND(0.6) |
| non-2378-HxCDD | ND(0.6) | ND(0.2) | ND(0.5) | ND(0.2) | ND(0.6) |
| 1234678-HpCDD | 3.4 | 2.3 | 2.3 | 2.6 | 3.3 |
| non-2378-HpCDD | 3.6 | 2.0 | 1.9 | 2.3 | 2.8 |
| OCDD | 60 | 28 | 33[37%]b | 41 | 43 |
| 2378-TCDF | 57 | 15 | 2.8 | 1.4 | 19 |
| non-2378-TCDF | 102 | 39 | 4.6 | 2.7 | 38 |
| 12378-PeCDD | 2.4 | 2.4 | ND(0.2) | ND(0.1) | ND(0.6) |
| 23478-PeCDD | 1.5 | 1.1 | ND(0.2) | ND(0.1) | ND(0.2) |
| non-2378-PeCDD | 8.8 | 4.2 | 1.7 | 4.8 | 3.8 |
| 123478-HxCDF | ND(0.4) | ND(1.2) | ND(0.4) | ND(0.2) | ND(0.3) |
| 123678-HxCDF | ND(0.1) | ND(0.3) | ND(0.4) | ND(0.2) | ND(0.3) |
| 234678-HxCDF | ND(0.4) | ND(0.3) | ND(0.4) | ND(0.2) | ND(0.3) |
| 123789-HxCDF | ND(0.1) | ND(0.3) | ND(0.4) | ND(0.2) | ND(0.3) |
| non-2378-HxCDF | 1.7 | ND(0.3) | ND(0.4) | ND(0.2) | ND(0.3) |
| 1234678-HpCDF | ND(0.6) | 0.8 | ND(0.3) | ND(0.4) | ND(2.1) |
| 1234789-HpCDF | ND(0.6) | ND(0.2) | ND(0.3) | ND(0.4) | ND(2.1) |
| non-2378-HpCDF | ND(0.6) | ND(0.2) | ND(0.3) | 1.0 | ND(2.1) |
| OCDF | ND(2.8) | 2.2 | 1.9 | 2.1 | ND(3.0) |
| Toxicity Equivalence | 28 | 8.1 | 2.0 | 0.6 | 8.8 |
| % Equivalence As 2378-TCDD/F | 94 | 91 | 97 | 89 | 99 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

Table 14 (Continued)

| Analyte | Mill E | Mill E (Replicate) | Mill F | Mill G | Mill H | MILL I |
|---|---|---|---|---|---|---|
| | | ( ng/kg, ppt ) | | | | |
| 2378-TCDD | 7.4 | 8.0 | 7.4 | 4.6 | 124 | 1.4 |
| non-2378-TCDD | ND(0.6)a | ND(0.6) | ND(0.5) | ND(0.4) | 7.0 | ND(0.2) |
| 12378-PeCDD | ND(0.2) | ND(0.2) | ND(0.3) | 0.5 | ND(1.5) | ND(0.2) |
| non-2378-PeCDD | ND(0.2) | ND(0.2) | ND(0.3) | ND(0.2) | 2.1 | ND(0.2) |
| 123478-HxCDD | ND(0.5)a | ND(0.3) | ND(0.4) | 0.4 | ND(0.2) | ND(0.4) |
| 123678-HxCDD | ND(0.5) | ND(0.3) | ND(0.4) | 0.7 | 1.6 | ND(0.4) |
| 123789-HxCDD | ND(0.5) | ND(0.3) | ND(0.4) | 0.5 | ND(1.1) | ND(0.4) |
| non-2378-HxCDD | ND(0.5) | ND(0.3) | ND(0.4) | 5.5 | 8.8 | 0.7 |
| 1234678-HpCDD | 2.4 | 5.3 | 3.7 | 8.4 | 3.6 | 6.6 |
| non-2378-HpCDD | 2.1 | 4.0 | 3.2 | 8.4 | 2.8 | 6.2 |
| OCDD | 40 | 81 | 47[36%]b | 65[38%]b | 45 | 81 |
| 2378-TCDF | 53 | 51 | 22 | 13 | 716 | 3.4 |
| non-2378-TCDF | 148 | 140 | 37 | 21 | 810 | 3.8 |
| 12378-PeCDD | ND(0.7) | ND(0.6) | ND(0.3) | 0.7 | 3.9 | ND(0.2) |
| 23478-PeCDD | ND(0.6) | ND(0.4) | ND(0.3) | ND(0.2) | 4.7 | ND(0.2) |
| non-2378-PeCDD | 17 | 3.1 | 2.2 | 7.7 | 9.0 | ND(0.2) |
| 123478-HxCDF | ND(0.2) | ND(0.2) | ND(0.3) | 0.0 | ND(0.6) | ND(0.3) |
| 123678-HxCDF | ND(0.2) | ND(0.2) | ND(0.3) | ND(0.2) | ND(0.2) | ND(0.3) |
| 234678-HxCDF | ND(0.2) | ND(0.2) | ND(0.3) | ND(0.2) | ND(0.4) | ND(0.3) |
| 123789-HxCDF | ND(0.2) | ND(0.2) | ND(0.3) | ND(0.2) | ND(0.2) | ND(0.3) |
| non-2378-HxCDF | ND(0.2) | 1.1 | ND(0.3) | 0.9 | 1.6 | 0.4 |
| 1234678-HpCDF | ND(0.1) | 0.6 | ND(0.5) | ND(1.2) | 0.8 | 0.7 |
| 1234789-HpCDF | ND(0.1) | ND(0.1) | ND(0.5) | ND(1.2) | ND(0.2) | ND(0.4) |
| non-2378-HpCDF | ND(0.1) | 1.5 | ND(0.5) | 2.3 | ND(0.2) | 1.7 |
| OCDF | 2.1 | 4.1 | 1.9 | 4.3 | 2.3 | 5.5 |
| Toxicity Equivalence | 13 | 13 | 9.8 | 6.5 | 198 | 1.9 |
| % Equivalence As 2378-TCDD/F | 99 | 99 | 99 | 90 | 99 | 92 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis.

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

Table 15 104 Mill Study Sludge Full Congener Analyses 1988-89

| Analyte | Mill A | Mill B | Mill C | Mill D | Mill D Replicate |
|---|---|---|---|---|---|
| | | (ng/kg, ppt) | | | |
| 2378-TCDD | 63 | 180 | 6.8 | 88 | 92 |
| non-2378-TCDD | ND(1.9)a | 74 | ND(1.5) | ND(1.5) | ND(1.5) |
| 12378-PeCDD | ND(4.7) | ND(7.8) | ND(2.2) | ND(2.5) | ND(3.1) |
| non-2378-PeCDD | 10 | ND(7.8) | ND(2.2) | ND(2.5) | ND(3.1) |
| 123478-HxCDD | ND(2.4)a | ND(3.5) | ND(1.7) | ND(4.0) | ND(4.8) |
| 123678-HxCDD | ND(2.4) | ND(3.4) | ND(1.7) | ND(2.7) | ND(4.8) |
| 123789-HxCDD | ND(3.2) | ND(2.1) | ND(1.7) | ND(4.0) | ND(4.8) |
| non-2378-HxCDD | ND(8.7) | 11 | 4.2 | 8.0 | 9.9 |
| 1234678-HpCDD | 18 | 35 | 21 | 34 | 35 |
| non-2378-HpCDD | 18 | 35 | 18 | 42 | 43 |
| OCDD | 263 | 677 | 335 | 719 | 687 |
| 2378-TCDF | 273 | 328 | 13 | 233 | 233 |
| non-2378-TCDF | 547 | 730 | 37 | 412 | 423 |
| 12378-PeCDD | 7.8 | 12 | ND(1.2) | 4.9 | 5.5 |
| 23478-PeCDD | 4.7 | 7.0 | ND(0.9) | 3.1 | 3.9 |
| non-2378-PeCDD | 16 | 28 | ND(2.5) | 14 | 12 |
| 123478-HxCDF | ND(1.7) | 4.8 | ND(0.9) | ND(1.9) | ND(2.6) |
| 123678-HxCDF | ND(1.7) | ND(1.7) | ND(0.9) | ND(1.2) | ND(1.8) |
| 234678-HxCDF | ND(1.7) | ND(1.9) | ND(0.9) | ND(1.2) | ND(2.6) |
| 123789-HxCDF | ND(1.7) | ND(1.9) | ND(0.9) | ND(1.2) | ND(2.6) |
| non-2378-HxCDF | 2.0 | ND(1.9) | ND(0.9) | 5.2 | 4.3 |
| 1234678-HpCDF | 3.5 | 5.5 | ND(3.6) | ND(0.4) | 6.0 |
| 1234789-HpCDF | ND(1.2) | ND(1.4) | ND(3.6) | ND(0.4) | ND(1.0) |
| non-2378-HpCDF | ND(1.2) | 5.7 | 4.8 | 1.0 | ND(1.0) |
| OCDF | 14 | 13 | 14 | 2.1 | 23 |
| Toxicity Equivalence | 94 | 218 | 8.6 | 114 | 118 |
| % Equivalence As 2378-TCDD/F | 97 | 97 | 94 | 97 | 97 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

Table 15 (Continued)

| Analyte | Mill E | Mill F | Mill G | Mill H | Mill I |
|---|---|---|---|---|---|
| | | (ng/kg, ppt) | | | |
| 2378-TCDD | 147 | 24 | ND(6.3) | 116 | 14 |
| non-2378-TCDD | ND(1.2)a | 837 | ND(6.3) | ND(1.1) | ND(1.1) |
| 12378-PeCDD | ND(7.2) | 28 | ND(1.4) | ND(2.9) | ND(1.6) |
| non-2378-PeCDD | 7.2 | 1280 | ND(1.4) | ND(2.9) | ND(1.6) |
| 123478-HxCDD | ND(3.7)a | 40 | ND(3.5) | ND(1.5) | ND(3.1) |
| 123678-HxCDD | ND(3.2) | 95 | ND(5.4) | ND(8.6) | ND(3.1) |
| 123789-HxCDD | ND(4.3) | 80 | ND(3.9) | ND(5.3) | ND(3.1) |
| non-2378-HxCDD | 14 | 2180 | 38 | 64 | ND(3.1) |
| 1234678-HpCDD | 80 | 490 | 136 | 37 | 39 |
| non-2378-HpCDD | 119 | 447 | 115 | 35 | 32 |
| OCDD | 1780 | 1090 | 1460 | 399 | 698[19%]b |
| 2378-TCDF | 1150 | 69 | 27 | 536 | 29 |
| non-2378-TCDF | 2310 | 650 | 48 | 830 | 109 |
| 12378-PeCDD | 22 | 21 | ND(1.2) | 6.2 | ND(1.2) |
| 23478-PeCDD | 18 | 38 | ND(1.6) | 5.3 | ND(1.3) |
| non-2378-PeCDD | 41 | 268 | ND(2.0) | 6.4 | 5.5 |
| 123478-HxCDF | ND(2.5) | 31 | ND(3.0) | ND(4.0) | ND(1.2) |
| 123678-HxCDF | ND(1.4) | 33 | ND(2.3) | ND(1.2) | ND(1.2) |
| 234678-HxCDF | ND(2.0) | 34 | ND(3.0) | ND(1.2) | ND(1.2) |
| 123789-HxCDF | ND(2.2) | ND(4.0) | ND(3.0) | ND(1.2) | ND(1.2) |
| non-2378-HxCDF | 19 | 219 | 21 | 19 | 3.2 |
| 1234678-HpCDF | 7.9 | 70 | 17 | 54 | 6.6 |
| 1234789-HpCDF | ND(1.4) | 10 | ND(1.6) | ND(1.4) | ND(4.3) |
| non-2378-HpCDF | 17 | 63 | 41 | 41 | 12.7 |
| OCDF | 35 | 60 | 84 | 168 | ND(54) |
| Toxicity Equivalence | 274 | 103 | 5.8 | 174 | 18 |
| % Equivalence As 2378-TCDD/F | 95 | 30 | 47 | 97 | 94 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

Table 16 104 Mill Study Effluent Full Congener Analyses 1988-89

| Analyte | Mill A | Mill B | Mill C | Mill D | Mill F |
|---|---|---|---|---|---|
| | | (pg/l, ppq) | | | |
| 2378-TCDD | 42[28%]b | 89[23%]b | ND(11)a | 86[35%]b | 12 |
| non-2378-TCDD | ND(3.0)a | 101 | ND(11) | 34 | 138 |
| 12378-PeCDD | ND(6.6)b | ND(13)[27%]b | ND(2.8) | ND(7.8) | ND(0.8) |
| non-2378-PeCDD | 15 | 19 | 9.6 | 50 | 130 |
| 123478-HxCDD | ND(12)[23%]b | ND(12)[19%]b | ND(6.6) | ND(9.3)[33%]b | ND(12) |
| 123678-HxCDD | ND(12) | ND(12) | ND(6.6) | ND(9.3) | ND(24) |
| 123789-HxCDD | ND(12) | ND(12) | ND(6.6) | ND(11) | ND(23) |
| non-2378-HxCDD | ND(12) | ND(12) | ND(6.6) | 43 | 360 |
| 1234678-HpCDD | 170[18%]b | 170[14%]b | 120[29%]b | 190[27%]b | 260[30%]b |
| non-2378-HpCDD | 120 | 120 | 80 | 120 | 160 |
| OCDD | 4600[8%]b | 3900[5%]b | 2100[10%]b | 3000[10%]b | 2600[10%]b |
| 2378-TCDF | 120[34%])b | 160[26%]b | 12 | 200[39%]b | 24 |
| non-2378-TCDF | 270 | 370 | 43 | 420 | 126 |
| 12378-PeCDD | ND(7.0) | ND(7.2) | ND(2.2) | ND(7.2) | 5.5 |
| 23478-PeCDD | ND(8.1) | ND(6.3) | ND(2.2) | ND(6.2) | 9.5 |
| non-2378-PeCDD | 30 | 21 | ND(2.2) | 28 | 49 |
| 123478-HxCDF | ND(5.2) | ND(6.2) | ND(5.8) | ND(4.8) | ND(14) |
| 123678-HxCDF | ND(5.2) | ND(6.2) | ND(5.8) | ND(4.8) | ND(7.1) |
| 234678-HxCDF | ND(5.2) | ND(6.2) | ND(5.8) | ND(4.8) | ND(8.2) |
| 123789-HxCDF | ND(5.2) | ND(6.2) | ND(5.8) | ND(4.8) | ND(2.5) |
| non-2378-HxCDF | ND(5.2) | ND(6.2) | ND(5.8) | 20 | 54 |
| 1234678-HpCDF | ND(22) | ND(21) | ND(13) | 21 | ND(23) |
| 1234789-HpCDF | ND(22) | ND(17) | ND(13) | ND(6.4) | ND(23) |
| non-2378-HpCDF | 35 | ND(21) | ND(13) | 79 | 36 |
| OCDF | 140 | 250 | 78 | 300 | 110 |
| Toxicity Equivalence | 60 | 111 | 4.6 | 114 | 25 |
| % Equivalence As 2378-TCDD/F | 89 | 95 | 26 | 95 | 58 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

Table 16 (Continued)

| Analyte | Mill E | Mill G | Mill H | Mill H Replicate | Mill I |
|---|---|---|---|---|---|
| | | ( ng/kg, ppt ) | | | |
| 2378-TCDD | 92 | 31[38%]b | 98[31%]b | 64 | 22[34%]b |
| non-2378-TCDD | 108 | 34 | 122 | 96 | 14 |
| 12378-PeCDD | ND(18)a | ND(9.6)a | ND(13) | ND(2.9)a | ND(25)[20%]b |
| non-2378-PeCDD | ND(18) | ND(9.6) | ND(13) | 22 | ND(25) |
| 123478-HxCDD | ND(17) | ND(19)[30%]b | ND(23) | ND(6.6)[31%]b | ND(12)[30%]b |
| 123678-HxCDD | ND(17) | ND(19) | ND(23) | ND(17) | ND(12) |
| 123789-HxCDD | ND(17) | ND(19) | ND(23) | ND(13) | ND(12) |
| non-2378-HxCDD | ND(17) | 80 | 42 | 60 | ND(12) |
| 1234678-HpCDD | 77 | 270[22%]b | 260[22%]b | 140[23%]b | 170[23%]b |
| non-2378-HpCDD | 73 | 160 | ND(27) | 90 | 130 |
| OCDD | 1000[33%]b | 4300[8%]b | 4200[8%]b | 2700[9%]b | 2700[9%]b |
| 2378-TCDF | 840 | 72 | 420 | 270 | 74 |
| non-2378-TCDF | 1460 | 128 | 450 | 390 | 126 |
| 12378-PeCDD | 36 | ND(3.4) | ND(22) | ND(3.3) | ND(4.3) |
| 23478-PeCDD | 33 | ND(3.4) | ND(22) | ND(4.4) | ND(4.3) |
| non-2378-PeCDD | 71 | ND(3.4) | ND(22) | 24 | ND(13) |
| 123478-HxCDF | ND(19) | ND(15) | ND(9.4) | ND(2.0) | ND(8.4) |
| 123678-HxCDF | ND(9.0) | ND(15) | ND(9.4) | ND(2.0) | ND(8.4) |
| 234678-HxCDF | ND(9.0) | ND(15) | ND(9.4) | ND(2.6) | ND(8.4) |
| 123789-HxCDF | ND(9.0) | ND(15) | ND(9.4) | ND(2.0) | ND(8.4) |
| non-2378-HxCDF | 31 | ND(15) | ND(9.4) | 14 | 7.6 |
| 1234678-HpCDF | 44 | 32 | ND(41) | ND(19) | ND(23) |
| 1234789-HpCDF | ND(14) | ND(12) | ND(41) | ND(5.4) | ND(23) |
| non-2378-HpCDF | 31 | 78 | 76 | 33 | 49 |
| OCDF | 190 | 240 | 320 | 160 | ND(180) |
| Toxicity Equivalence | 197 | 46 | 147 | 95 | 34 |
| % Equivalence As 2378-TCDD/F | 89 | 83 | 95 | 95 | 87 |

a--ND designates "not detected" above the minimum detectable concentration shown in parenthesis

b--Internal standard recovery below 40%. Since there is no clear consensus in the scientific community on minimum required for the higher congeners, no mimimum recovery criteria have been established. The number in [] is the internal standard recovery.

# APPENDIX A
# 104 MILL STUDY AGREEMENT

# U.S. EPA - PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

## I. Background

In the course of the National Dioxin Study, 2,3,7,8-tetrachlordibenzo-p-dioxin ("2378-TCDD") was detected in fish and river sediment samples collected downstream from some pulp and paper mills located in various parts of the country. In addition, 2378-TCDD and other polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) were discovered in parts-per-trillion concentrations in wastewater treatment plant sludges from bleached kraft paper mills. In order to assess further the generation and treatment of these compounds at bleached kraft pulp and papermaking operations, EPA, the American Paper Institute (API), and the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) entered into an agreement, dated June 20, 1986, to jointly perform the "USEPA/Paper Industry Cooperative Dioxin Screening Study" at five bleached kraft mills (the "Five Mill Study").

The results of the Five Mill Study indicated that dioxin was present in the treated effluent at three of the five mills, in wastewater treatment sludges of all five mills, and in bleached pulps at four of the mills. The Five Mill Study data base, while a solid start, does not provide sufficient data to characterize the entire industry for all of the federal government's varied regulatory responsibilities. EPA believes there is a need to assess, as quickly as possible, the extent to which chlorinated dioxins or furans are present in bleached pulp mill effluent, sludge, and pulp. In addition, state environmental agencies will in many cases wish to obtain such data in order to determine the need for action under state environmental laws.

In addition to the information which EPA seeks in order to characterize rapidly dioxin generation at all mills bleaching chemical wood pulp with chlorine or chlorine derivatives, API and NCASI have decided to conduct additional and more detailed investigations, using professional researchers working for NCASI, to characterize a subset of those mills. EPA encourages this additional investigation and has attempted to incorporate the industry plans into EPA's own information collection plans. EPA understands NCASI's desire to pursue this more intensive study without undue duplication of effort and without unreasonably extending the time required to obtain a rapid characterization of all such mills.

There is a limitation on the number of analyses per week for 2378-TCDD and other chlorinated dioxins and furans which can be carried out with the necessary level of precision and accuracy using existing independent laboratory capacity. In addition, there are numerous other demands for such analytical work, such as treatability studies, migration studies, process studies, and so forth, beyond the analytical needs for the cooperative study outlined herein.

II. Purpose

The parties agree that use of a cooperative study to provide these data is the most efficient strategy for meeting EPA's responsibilities in light of the need for rapid data development and comprehensively organized allocation of limited laboratory capacity. Further, use of a cooperative agreement will ensure that the sampling and analyses are conducted in a consistent manner with EPA-approved quality assurance/quality control measures.

Collection of these data will assist EPA to fulfill its regulatory responsibilities. Under the Clean Water Act (CWA), EPA is required to promulgate and update effluent limitations guidelines and standards and other water quality regulations, as well as to issue NPDES permits where states are not authorized to do so. Under the Toxic Substances Control Act (TSCA), EPA is authorized to regulate various activities which may present an unreasonable risk of injury to health or the environment as well as to establish other types of controls. In furtherance of these functions, the CWA and TSCA authorize EPA to gather information and require the submission of test, monitoring, and other types of data.

While API and the participating companies do not necessarily agree that EPA has authority to demand all of the information provided in this cooperative study, API and the participating companies have agreed to cooperate with EPA in order to assist the Agency to evaluate dioxin generation at pulp and paper mills and to assure that the needed information is collected in an efficient, orderly way. (As used in this Agreement, "participating companies" refers to those companies which are signatories to this Agreement.)

III. General Project Organization and Responsibilities

1. API Responsibilities

1.1 API has identified, on Attachment 4, all mills in the United States which are known to operate chemical wood pulping mills bleaching with chlorine or chlorine derivatives.

1.2 API shall use its best efforts to secure the participation in this Agreement of all companies which own or partially own any of the mills listed in Attachment 4, regardless of whether those companies are members of API or NCASI.

2. Participating Companies' Responsibilities

2.1 Participating companies will provide the bleach plant information described in Attachment 1 and the wastewater treatment and sludge management information described in Attachment 3 to NCASI for each mill identified in Attachment 4 in order for NCASI to make timely submissions of aggregated mill data according to the schedule set forth in Paragraph 3, below. This provision does not require the generation of any new analytical data but rather is intended to be based on available information or estimates.

2.2 Participating companies, when requested by NCASI, shall collect effluent, bleached pulp, and wastewater treatment plant sludge samples, following the sampling program described in Attachment 2, for each mill listed on Attachment 4, and shall submit these samples to NCASI no later than the date established by NCASI as necessary to meet its data analysis and reporting commitments in Paragraph 3, below. Prior to initiation of the sampling program at each mill, the person responsible for the sampling program shall assure that applicable bleach plant monitoring and reporting systems are operational and in good working order so that the data requested in Attachment 2, Item 5 can be obtained as accurately and completely as possible within the context of existing monitoring systems at the mill. The person responsible for the sampling program shall also assure that, during the sampling program, data and information are collected in accordance with Attachment 2 and with the sampling protocol which is to be developed by NCASI and will be subject to EPA review upon request.

2.3 Each participating company shall, not later than 30 days after the Agreement takes effect, submit to NCASI the results of any analyses for chlorinated dioxins or chlorinated furans which that company has obtained for samples of wastewaters (treated and untreated), wastewater treatment sludges, bleached or partially bleached pulps, other process raw materials or chemical additives used in the process of manufacturing bleached pulp, treated process (intake) waters, and any fish or environmental media, which have been obtained from any mill identified in Attachment 4 that is owned, partially owned, or operated by that company.

2.4 Participating companies shall provide EPA and state environmental agency representatives with access to any mill listed in Attachment 4 in order to observe the sampling being conducted pursuant to Paragraph 2.2, above.

2.5 Participating companies shall, at the time any data are submitted to NCASI, submit to NCASI in writing any claim of confidentiality which they intend to make for such data. Such submission shall also designate the company representative to be contacted about any matters concerning the confidentiality claim. Participating companies agree not to assert any claim of confidentiality for analytical data on treated or untreated wastewater or wastewater treatment sludge. Participating companies may also choose to send information directly to EPA rather than through NCASI for reasons of confidentiality, or they may seek to enter into separate confidentiality agreements with EPA, to the extent permitted by 40 C.F.R. Part 2, to supplement this Agreement.

2.6 Whenever any mill submits information to NCASI or EPA pursuant to this Agreement, that submittal shall be treated as information submitted under 40 C.F.R. §122.22(b) and shall be accompanied by a written certification to EPA in accordance with 40 C.F.R. §122.22.

3. NCASI Responsibilities

3.1 To insure that analytical testing will not be influenced in any way by sample origin and to protect possible confidential business information, samples submitted to analytical laboratories and information reported to EPA by NCASI will be identified by code numbers. No later than 15 days after the Agreement takes effect, NCASI shall assign unique code numbers to the mills identified in Attachment 4. Data shall be reported by NCASI to EPA using the mill code numbers, but NCASI shall provide EPA with a list of the mill code numbers and the identity and location of the mills which they represent within 15 days after the Agreement takes effect.

3.2 NCASI shall compile, review for completeness, and submit to EPA the information described in Paragraphs 1, 2, and 8 of Attachment 1 and Paragraph 1 of Attachment 3 no later than 60 days after the Agreement takes effect. (EPA recognizes that, due to this tight schedule, data for a few mills might still be unclear and unverified by this deadline. These data will be submitted as soon thereafter as feasible, but not later than 120 days after the Agreement takes effect.

3.3 NCASI shall compile, review for completeness, and submit to EPA the information described in Paragraphs 3-7 of Attachment 1 no later than 120 days after the Agreement takes effect. (EPA recognizes that, for reasons of confidentiality, some mills may choose to submit this information directly to EPA.) NCASI shall compile, review for completeness, and submit to EPA the information described in Paragraph 2 of Attachment 3 no later than 90 days after the Agreement takes effect.

3.4 Within 30 days after the Agreement takes effect, NCASI shall submit to EPA a description of a more intensive study of a group of approximately 25-30 mills, to be conducted by NCASI researchers. This submittal shall also include a list of the mills to be examined as part of the NCASI study (the "Intensive Study Group"). Within twenty-one (21) days of receipt of NCASI's study plans, EPA shall submit comments to NCASI on the plan and on the selection of mills to be included in the Intensive Study Group. NCASI shall consider those comments and, if appropriate, incorporate them into the final study plan. NCASI shall provide EPA with a copy of the final study plan within twenty-one (21) days of receipt of EPA's comments.

3.5 The information collected by NCASI at mills in the Intensive Study Group will go beyond that described in Attachment

2 to this Agreement; however, all of the samples and operating information described in Attachment 2 shall be collected by NCASI at those mills and shall be reported to EPA in the same manner as all of the other mills listed on Attachment 4, as described in Paragraphs 3.6 and 3.7. The Parties anticipate, however, that, due to the limited number of experienced research teams available and the greater number of samples to be taken at mills in the Intensive Study Group, collection of samples from mills in the Intensive Study Group will not proceed as rapidly as at the remainder of the mills listed in Attachment 4. EPA has provided, in Attachment 5, a list of mills for priority sampling and analysis. To the extent that any of those mills also are included in the Intensive Study Group, EPA and NCASI will meet to resolve any differences concerning the priority in which mills should be sampled. NCASI will also, subject to EPA concurrence, prioritize the mills not on Attachment 5 or in the Intensive Study Group, which will collect their own samples, to be analyzed after those from mills listed in Attachment 5. That priority list shall be designed to assure, to the extent possible, that a range of mills with high, medium, and low usage of chlorine or chlorine derivatives are analyzed early on.

3.6 NCASI shall follow the protocols established in the Five Mill Study for the collection of the 5-day composite samples collected pursuant to Paragraph 2.2., with sample sizes being adjusted to match the analytical protocols. Pulp and sludge samples shall be processed (i.e., dried, homogenized, and split) prior to being submitted for analysis, using the procedures in Attachment 7. NCASI shall archive at least two (2) aliquots of each composite pulp and wastewater sludge sample for a period of one year for possible future analysis. NCASI shall submit those samples to analytical laboratories according to a priority to be established in writing by agreement between EPA and NCASI. Beginning 60 days after the Agreement takes effect, such samples shall be submitted to analytical laboratories at an average rate of not less than 35 per week. Samples shall be prepared and analyzed for 2378-TCDD and 2378-TCDF in strict accordance with the analytical protocols specified in Attachment 1 of the quality assurance project plan for the U.S. EPA/Paper Industry Cooperative Dioxin Screening Study (copy attached), or using an analytical protocol acceptable to all parties which has been demonstrated to meet the desired sensitivity and QA/QC objectives.

a. Analytical objectives

The analytical objectives for detection levels of 2378-TCDD and 2378-TCDF for these analyses are as follows:

| | 2378-TCDD | 2378-TCDF |
|---|---|---|
| Bleached Pulp and Wastewater Sludge | 1 ppt | 1 ppt |
| Process Wastewater Effluents | 0.01 ppt | 0.01 ppt |

EPA recognizes that it may not be possible to achieve the above detection levels for all samples. NCASI shall establish, in connection with the affected mills, a sampling schedule to assure that samples are available to be analyzed as quickly as laboratory capacity permits. As requested by EPA, to the extent possible pulp and wastewater samples gathered pursuant to Paragraph 2.2 will be analyzed and reported before sludge samples from those mills. NCASI will assure that, for each ten (10) samples of a given matrix, at least one field or laboratory duplicate sample and one matrix spiked sample will be analyzed.

b. Interlaboratory comparisons

At the outset of the study NCASI will send one duplicate sample each of effluent, sludge, and pulp from each of 9 mills to two laboratories for inter-laboratory comparison. In the event these inter-laboratory comparisons demonstrate that these laboratories do not provide comparable analytical results, the sampling and analysis schedule set forth in this Agreement shall be deferred until EPA and NCASI can resolve these discrepancies.

c. Analysis for other PCDDs and PCDFs

At EPA's request, NCASI shall have analyses of other PCDDs and PCDFs conducted on samples of bleached pulp, treated wastewater effluent, and wastewater sludge from up to nine pulp and paper mills. The samples shall be analyzed for total TCDDs, PeCDDs, HxCDDs, HpCDDs, and OCDD; and total TCDFs, PeCDFs, HxCDFs, HpCDFs, and OCDF. Depending upon the results, NCASI shall have conducted at EPA's request isomer-specific analyses of selected PCDDs and PCDFs, along with isomer-specific 2378-TCDD and 2378-TCDF and with individual quantitation of peaks which elute at the same retention time as the 2,3,7,8-substituted isomers using GC columns which are generally believed to be the most isomer-specific. It is understood by both parties that there are no analytical protocols for these determinations which have been validated in advance for pulp or for pulp and paper industry sludges or effluents. Furthermore, it is understood that the analytical detection limits for these determinations are likely to be higher than the target detection limits for 2378-TCDD and 2378-TCDF. Accordingly, specific QA/QC criteria will not be established for the isomer-specific analyses. The parties agree that samples for the other PCDDs and PCDFs analyses from the nine mills shall not exceed 35 in number.

3.7 Laboratories shall be requested to provide to NCASI written analytical results, including worksheets and quality assurance/quality control data, for the samples described in Attachment 2 not later than thirty (30) days after receipt of the samples by the laboratory. Within fourteen (14) days of receipt of these data, NCASI shall review the data and determine whether the analytical testing results meet the identification and quantitation criteria set forth in Attachment 6. All analytical results from the sampling described in Attachment 2 which meet these criteria shall be forwarded to EPA, identified by mill code number and sample type, in a monthly report to be submitted within 120 days after the Agreement takes effect and every 30 days thereafter (except that an interim report shall also be submitted on or about 15 days after the initial report). For each sample, these reports shall provide, in a format similar to that described in Attachment 6, the concentration of 2378-TCDD and 2378-TCDF, <u>or</u> the analytical detection limit for each compound, the percent recovery on the internal standard for each compound, and the monitored ion ratio for each compound. The same data shall be provided for duplicate, field blank, and spiked samples. If an analytical result does not meet the identification and quantitation criteria described in Attachment 6, NCASI may have the sample reanalyzed before any data are reported, but all analytical data received from the laboratories must be reported to EPA as described in Attachment 6. (EPA reserves the right to "audit" selected analytical results, in which case NCASI shall provide EPA with access to all laboratory documentation supporting the analyses.) The reports to EPA described in this paragraph shall also indicate the number of samples which have been transmitted to the analytical laboratory(ies) but for which results have not yet been received. Within thirty (30) days after submission of each monthly data report described in this paragraph, NCASI shall submit to EPA the information described in Paragraph 5 of Attachment 2 for each mill for which analytical results for the associated samples were first provided in that monthly data report.

3.8 NCASI shall bear the costs of storage, initial sample preparation, shipment to the analytical laboratory, and analysis for all samples collected pursuant to this Agreement.

3.9 Not later than 60 days after the Agreement takes effect NCASI shall briefly review the information submitted to it pursuant to Paragraph 2.3 of this Agreement and shall submit to EPA a list, coded by mill, of the type and amount of data, by media, received. That list shall be accompanied by an estimate of the time required for NCASI to review all of the data, compile it, and submit it to EPA along with appropriate qualifications as to the validity or significance of the data. (EPA does not agree in advance to concur with any qualifications NCASI may assign to the data.) EPA and NCASI will then agree on a reasonable deadline for the submission of this compiled and annotated data, but such deadline shall not be later than 150 days after the Agreement takes effect.

3.10 As soon as practicable after receipt of all analytical data for sampling performed at mills in the Intensive Study Group, but no later than 545 days after the Agreement takes effect, NCASI shall submit to EPA a comprehensive report setting forth the conclusions drawn from NCASI's work at mills in the Intensive Study Group and providing all supporting analytical data. It is presently anticipated that this report should be available within 365 days after the Agreement takes effect. (This Paragraph does not extend the deadlines for reporting any of the information which EPA requested and which is described in Attachments 1-3 to this Agreement.)

3.11 On or before submitting any analytical data or other mill information to EPA pursuant to this Agreement, NCASI shall supply to EPA the mill certification required by Paragraph 2.6. NCASI agrees that, when submitting any data or other information to EPA, it will forward to EPA any claim of confidentiality which has been made by the company submitting such data to NCASI.

3.12 In addition to the work pursuant to this Agreement, NCASI has been conducting and will continue to conduct considerable research into the causes and the significance of dioxin formation in the bleaching process. NCASI agrees to submit to EPA, at a frequency not less than quarterly, beginning ninety days after the Agreement takes place and running until 15 months after that date, reports on the progress of this ongoing industry research program, which includes research on wastewater treatability, effects of process variables on dioxin generation, assessment of exposure to dioxin from pulp mill waste streams and products, and research on a pharmacokinetic risk assessment model for 2378-TCDD. These reports shall also describe progress in NCASI sampling and analysis for the mills in the Intensive Study Group.

4. EPA Responsibilities

4.1 Based on current information, EPA believes that the information described in this Agreement should be sufficient to characterize dioxin generation at the mills listed in Attachment 4. However, nothing in this Agreement shall be construed to limit in any way EPA's authority to require the submission of information not covered by this Agreement, to respond to conditions which EPA believes constitute an imminent and substantial endangerment to human health or the environment, or to take any action authorized under law, including permitting or enforcement under the Clean Water Act.

4.2 EPA shall consider the timely and complete implementation of this Agreement to constitute a sufficient and timely response by the participating companies to a request pursuant to Section 308 of the Clean Water Act, Section 4 of TSCA, or any other authorities for the same information on dioxin generation at the mills listed on Attachment 4. If any mill has not submitted the data subscribed in Paragraph 2.3 and Attachments 1-3 in a timely and complete manner, the Parties recognize that EPA shall use all available EPA authorities to collect the data. API, NCASI, and the participating companies waive any right they may have to challenge any Section 308 letter sent as a result of alleged failure to submit timely and complete data as described above on the grounds that EPA does not have authority under Section 308 to collect such data. EPA recognizes that API, NCASI, and the participating companies waive the opportunity to challenge EPA's statutory authority to collect such data only with respect to any Section 308 letter arising out of an alleged failure to submit the data described in this Agreement in a timely and complete manner, and API, NCASI, and the participating companies have not waived their rights to challenge on any ground any Section 308 letter issued for any other data or in any other context.

4.3 EPA and any EPA contractor will treat all information for which a claim of confidentiality has been asserted in accordance with the procedures of 40 C.F.R. Part 2, Subpart B. The EPA contractor shall require any employee who may receive data obtained pursuant to this Agreement for which a claim of confidentiality has been asserted to sign a confidentiality agreement pursuant to 40 C.F.R. § 2.301(h). Violation of such an agreement may result in the imposition of penalties referenced in 40 C.F.R. § 2.211, including possible criminal prosecution for willful violation.

4.4 EPA will protect confidential business information in accordance with 40 C.F.R. Part 2, Subpart B. Although requested by API and NCASI to provide additional procedures beyond those in 40 C.F.R. Part 2 to protect business information determined by EPA to be confidential, EPA was unwilling to do so.

4.5 EPA shall choose the appropriate manner in which to release any information submitted to it pursuant to this Agreement after considering the confidentiality provisions of applicable federal environmental statutes and EPA regulations.

5. API, EPA, NCASI and the participating companies agree that:

5.1 References to collection of data from mills listed in Attachment 4 to this Agreement are not meant to require additional sampling and analysis at the mills which were the subject of the Five Mill Study, since samples similar to those described in this Agreement have already been collected and analyzed for those mills. Those mills, and any others which EPA agrees are entitled to similar treatment because they have satisfactorily completed an equivalent comprehensive study, are still required, however, to submit the information described in Paragraphs 2.1 and 2.3.

5.2 Wherever this Agreement requires notification of one of the Parties or submission of data to EPA, the notification or submission shall be addressed:

For EPA, to:

Mr. Thomas O'Farrell (WH-552)
Chief, Consumer Products Branch
Industrial Technology Division
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

For API, to:

Mr. Michael C. Farrar
Vice President, Environmental and Health Program
The American Paper Institute
Suite 210
1250 Connecticut Avenue, N.W.
Washington, D.C. 20036

For NCASI, to:

Dr. Isaiah Gellman
President
National Council of the Paper Industry
for Air and Stream Improvement
260 Madison Avenue
New York, New York 10016

If it becomes necessary to replace one of these contact persons, the affected Party shall transmit to the other Parties notice of the replacement within five (5) days.

5.3 The Parties recognize that EPA or other federal agencies may desire additional information related to PCDD and PCDF formation in bleached pulp mills outside the scope of the information covered by this Agreement. The Parties recognize that it may be appropriate at some point in the future to enter into further cooperative efforts in addition to this Agreement to address those other information needs or to reflect ongoing research.

5.4 The Parties anticipate that it may be necessary to make minor modifications to the technical requirements and deadlines contained in this Agreement. Such minor modifications can be made by unanimous written consent of the EPA, API, and NCASI representatives listed in Paragraph 5.2 and shall be binding on all participating companies.

5.5 This Agreement shall become effective upon signature of all Parties to the Agreement and shall terminate 575 days after the Agreement takes effect, except that the provisions of Paragraphs 4.1 through 4.4, and the requirements in Paragraph 3.6 and Attachment 2 for retention of samples, shall remain in effect.

The undersigned parties hereby consent to this Agreement.

AMERICAN PAPER INSTITUTE, INC.

By: ______________________ April 1, 1988
Red Cavaney Date
President

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

By: I. Isaiah Gellman April 1, 1988
Isaiah Gellman Date
President

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

By: William A. Whittington
William A. Whittington
Director
Office of Water Regulations and Standards

April 25, 1988
Date

By: Charles L. Elkins
Charles L. Elkins
Director
Office of Toxic Substances

April 25, 1988
Date

Companies, as reflected on the next page, owning or operating chemical wood pulping mills bleaching with chlorine or chlorine derivatives:

Scott Paper Co.
- Everett, WA
- Hinckley, ME (S.D. Warren)
- Mobile, AL
- Muskegon, MI (S.D. Warren)
- Westbrook, ME (S.D. Warren)

Simpson Paper Co.
- Anderson, CA (Simpson Paper Co.)
- Fairhaven, CA (Simpson Paper Co.)
- Pasadena, TX (Simpson Pasadena Paper Co.)
- Tacoma, WA (Simpson Tacoma Kraft Co.)

St. Joe Paper Co.
- Port St. Joe, FL

Stone Container Corp.
- Missoula, MT
- Panama City, FL
- Snowflake, AZ

Temple-Eastex, Inc.
- Evandale, TX

Union Camp Corp.
- Eastover, SC
- Franklin, VA

Westvaco Corp.
- Covington, VA
- Luke, MD
- Wickliffe, KY

Weyerhaeuser Co.
- Cosmopolis, WA
- Everett, WA
- Longview, WA
- New Bern, NC
- Plymouth, NC
- Rothschild, WI

Willamette Ind.
- Hawesville, KY

<u>Non-API Members</u>:

Alaska Pulp Corp.
- Sitka, AK

Badger Paper Mills, Inc.
- Peshtigo, WI

Kimberly-Clark Corp.
- Coosa Pines, AL

Lincoln Pulp/Paper
- Lincoln, ME

Wausau Paper Mills Co.
- Brokaw, WI

<u>Summary</u>

| | | |
|---|---|---|
| API Members | 37 Companies | 98 Mills |
| Non-API Members | 5 Companies | 5 Mills |
| TOTAL | 42 Companies | 103 Mills |

## ATTACHMENT 5

## EPA LIST OF MILLS FOR PRIORITY SAMPLING

| Company | Location | Number |
|---|---|---|
| Alabama River Pulp | Claiborne | AL0025968 |
| Boise Cascade Corp. | Jackson | AL0002755 |
| Boise Southern | DeRidder | LA0007927 |
| Boise Cascade Corp. | Rumford | ME0002054 |
| Buckeye Cellulose (P & G) | Oglethorpe | GA0049336 |
| Champion Intl. Corp | Catonment | FL0002526 |
| Consolidated Papers, Inc. | Wisc. Rpds | WI0037991 |
| Container Corp. of Amer. | Brewton | AL0002682 |
| Federal Paperboard Co. | Augusta | GA0002801 |
| Federal Paperboard Co. | Riegelwood | NC0003298 |
| Georgia-Pacific Corp. | Crossett | AR0001210 |
| Georgia-Pacific Corp. | Woodland | ME0001872 |
| Gulf States Paper Co. | Demopolis | AL0002828 |
| Hammermill Papers Group | Selma | AL0003018 |
| Hammermill Papers (PT) | Erie | PA0000124 |
| International Paper Co. | Natchez | MS0000213 |
| International Paper Co. | Moss Pt | MS0002674 |
| International Paper Co. | Bastrop | LA0007561 |
| International Paper Co. | Pine Bluff | AR0001970 |
| ITT Rayonier, Inc. | Jesup | GA0003620 |
| James R. Dixie/Northern | Butler | AL0003301 |
| Leaf River Forest Prod. | New August | MS0031704 |
| The Mead Corp. | Kingsport | TN0001643 |
| Nekoosa Papers Inc. | Nekoosa | WI0003620 |
| Pope & Talbot, Inc. | Halsey | OR0001074 |
| S.D. Warren (Scott P) (PT) | Muskegon | MI0001210 |
| S.D. Warren (Scott P) | Hinckley | ME0021521 |
| Simpson Paper Co. | Anderson | CA0004066 |
| Union Camp Corp. | Franklin | VA0004162 |
| Weyerhaeuser Co. | New Bern | NC0003191 |

## ATTACHMENT 6

## IDENTIFICATION AND QUANTITATION OF 2378-TCDD AND 2378-TCDF

The criteria for identification and quantitation of 2378-TCDD and 2378 TCDF are as follows:

| 2378-TCDD | | 2378-TCDF | |
|---|---|---|---|
| Ion Ratio 320/322 | 0.65-0.89 | Ion Ratio 304/306 | 0.65-0.89 |
| % Recovery Internal Standard | 40-120% | % Recovery Internal Standard | 40-120% |

If an analytical result does not meet the QA/QC criteria described in Attachment 6, NCASI will review the analytical data received from the contract laboratory to determine what corrective steps would be appropriate. If internal standard recoveries are below 20 percent, the analysis will be repeated. If, after two analyses, the internal standard percent recovery is not greater than 20 percent, both analyses of the sample shall be reported as PEQ (present, estimated quantitation) if the analyte was positively identified or PND (probably not detectable) with the estimated detection limit indicated in parentheses. The respective ion ratio and internal standard recovery for each analysis shall also be reported.

All 2378-TCDD and 2378 TCDF analytical data generated by NCASI pursuant to this Agreement shall be reported to EPA in a format similar to the following:

| Sample ID Number | Matrix | 2378 TCDD | Ion Ratio | Percent Recovery | Laboratory and Laboratory Report Date | 2378 TCDF | Ion Ratio | Percent Recovery | Laboratory and Laboratory Report Date |
|---|---|---|---|---|---|---|---|---|---|
| | Pulp | | | | | | | | |
| | Wastewater | | | | | | | | |
| | Sludge | | | | | | | | |

## ATTACHMENT 7

## NCASI SAMPLE HANDLING AND PROCESSING PROTOCOL

### SAFETY GUIDELINES

The analyst should be familiar with the General Laboratory Safety Rules, the Laboratory Work Practice Guidelines and the location and proper use of all safety equipment throughout the building (e.g. fire extinguishers, respirators, spill kits, etc.). The following Dioxin general lab procedures recommends the use of specific safety equipment during various phases of processing. Included is the use of fume hoods for solvents or the processing of samples with nuisance odors and dust masks to prevent the inhalation of particulate matter.

### GENERAL LAB PROCEDURES

Under no circumstances should a sample be touched, stored or in any way come in contact with any materials other than those prescribed below and then only after they have been properly prepared. Aluminum foil or unpowdered latex gloves require no pretreatment but fresh foil or a new pair of gloves should be used for each situation.

### I. CLEANING PROCEDURES

A. Solvent Cleaning

All materials (except aluminum foil and latex gloves) which come in contact with the sample (restricted to glass, stainless steel and Teflon) shall be solvent cleaned. Only Teflon squeeze bottles are to be used.

The following cleaning procedure will be followed:

(1) Soap and tap water wash all items using Pierce RBS-35 soap (20 mL RBS-35 per liter of tap water). Rinse with tap water following by deionized water.

(2) Methanol (Burdick and Jackson) rinse.

(3) Acetone (Burdick and Jackson) rinse.

(4) Methylene chloride (Burdick and Jackson) rinse.

(5) Air dry.

Used solvents should be stored in separate bottles marked "Used Methanol," "Used Acetone," and "Used DCM." Conduct solvent rinsing in a hood.

B. Glove Box Cleaning Procedure

The following cleaning procedure should be used prior to and between each sample when using the glove box for sample grinding or sample splitting:

(1) Vacuum all interior surfaces of the glovebox.

(2) Wipe down all inside surfaces with a wet sponge.

(3) Dry the glove box using a squeegee. Use a sponge to remove excess $H_2O$ from floor of glove box. If necessary an electric blow dryer can be used to speed up the drying process.

(4) The neoprene glove box sleeves will be vacuumed, wet wiped with a sponge and air dried. A clean pair of latex gloves will be placed over them prior to processing any sample.

C. Cleaning of Drying Cabinets

The drying cabinets should be cleaned between usage by vacuuming, wiping all interior surfaces with a wet sponge, and then should be left to air dry. The vent will be wiped clean with a wet sponge monthly. More frequent cleaning is required if the analyst observes accumulated dust or particulate between cleanings.

D. Cleaning of Blender Motor

The blender motor should be dismantled and cleaned monthly or any time the blender is dismantled for maintenance.

E. Laboratory Cleaning

Every two weeks the analyst should observe the general cleanliness of the laboratory and look for accumulations of dust or particulate in the room. Where possible wipe surfaces with a wet sponge and maintain an uncluttered work area.

## II. RECORD KEEPING

All processing of any dioxin samples should be described in the appropriate "Project Lab Book" in ink. The West Coast sample control number should be noted and should precede all other sample identification information (such as dates and sample codes). The processor must date and initial each entry corresponding to a processing step.

## III. SAMPLE HANDLING

A fresh pair of unpowdered latex gloves should be used for each sample and should be discarded after use. Reasonable efforts should be taken to protect samples from the direct light. Thus the lights should be turned off in cabinets used for drying samples except when required for handling and inspection. A dust mask should be worn during any processing where the inhalation of particulate matter is possible (e.g. during grinding of samples). Samples producing a nuisance odor should be handled with proper ventilation.

## IV. SAMPLE PROCESSING (DRYING AND GRINDING)

The following is a general procedure for processing samples that require drying and grinding. All air drying of samples must be done in a drying cabinet. When air drying samples the hood should be turned on and the doors closed. During the evenings when the janitors are scheduled to come in or when activity in the room may increase particulate levels in the air, turn the hood off with the doors closed. Samples are placed in the cabinets beginning with the top shelf until all shelves are full. If samples dry at varying rates no additional samples will be added until the last sample is dry and the cabinet is cleared. The samples on each shelf are segregated by a physical barrier.

### A. Blanks

An 8" x 10" Gelman type A glass fiber filter sheet should be placed in the center of the samples placed in the cabinets for drying. The filter sheet should not be pre-treated. Place the filter sheet on a piece of aluminum foil, edges folded up and label the foil with the date and time exposed in the laboratory. Barriers should separate the blank from samples on the same shelf in a manner analogous to the way samples are segregated. At the conclusion of drying of all the samples in the cabinet, the blank should be folded so as to cover the exposed upper surface and should be wrapped in aluminum foil until it is blended. Just prior to blending, the blank filter should be torn into small pieces and placed in the blender. Blend as described in Section IV Part D. Wrap the entire blended blank filter (i.e. do not split the blended filter) in aluminum foil and place the foil packet into an I-Chem bottle. Do not assign a sample code to the blank until it has been put into the I-Chem bottle. The blank sample code is the next number in sequence in the West Coast sample sequence log book. Record the blank preparation, cabinet number, glove box number, the dates exposed, blended and bottled, and sample code assigned in the appropriate Project Lab Book. Record the Project Lab Book page reference number in the NCASI West Coast Dioxin Sample Sequence Log Book.

B. Sample Preparation Procedures

(1) Pulp

Remove the pulp from the sample jar and hand squeeze out as much water as possible, discarding the water. Break the sample into small pieces (about dime size), lay out on a stainless steel screen supported about 1 cm above a sheet of aluminum foil and place the sample in a drying cabinet. The size of the foil should at least equal the area of the screen to catch and fines that may fall through. Wooden dowels wrapped in fresh aluminum foil are used to support the screen over the foil. Save the sample bottle, leaving the cap off until the inside moisture evaporates, for NCASI sample archives.

Label the foil with the West Coast control number and the time and date the sample was laid out in the drying cabinet. This information and the drying cabinet number should also be recorded in the appropriate Project Lab Book.

Continue with drying procedures Section IV, Part C.1.

(2) Sludges

Remove the sample from the jar and break into small pieces (about dime size), distribute uniformly on a stainless steel screen supported about 1 cm above a sheet of aluminum foil and place in a drying cabinet. The size of the foil should at least equal the area of the screen to catch any fines that may fall through. Wooden dowels wrapped in aluminum foil can be used to support the screen over the foil. Save the sample bottle, leaving cap off until inside moisture evaporates, for NCASI sample archives.

Continue with drying procedures Section IV, Part C.1.

C. Drying Procedure

On a daily basis, check to see if the sample is completely dry and if not turn the material and further break it up into smaller pieces to facilitate drying.

When the sample is completely dry, fold aluminum foil over the sample to cover it while waiting to grind. When screens are used transfer the sample to the aluminum foil base and wrap for grinding. Record the date and time the sample was wrapped up. If the dried sample is not ground immediately store the covered sample in the dry sample storage cabinet.

Grind the dried sample following General Procedure Section IV, Part D.

D. Grinding Samples - The grinding (or blending) of a dried sample should be conducted in the glove box. The working surface of the glove box should be covered or lined with aluminum foil. The door to the glove box room should be closed and traffic through the room minimized. The processes of air drying and blending will be separated by as many physical barriers as possible (i.e. separated on different floors).

(1) Blend the entire sample in a properly cleaned blender (see Section I). Be sure not to add too much sample into the blender at one time otherwise blending will not be uniform and the blender motor may overheat causing fragments of the blender to mix into the sample. To check for overheating press the bottom of the blender assembly with gloved hands. If the assembly feels warm discontinue grinding until cool. Place the blended sample on a sheet of aluminum foil in the glove box.

(2) Thoroughly mix the blended sample, using gloved hands or a stainless steel spoon, by turning the entire sample at least three times, then form into a conical pile. Carefully flatten the conical pile to a uniform thickness and diameter (as wide as spatially possible) by pressing down the apex. Divide the flattened mass into four equal quarters. Refer to ASTM "Standard Methods for Reducing Field Samples of Agregate to Testing Size."

(3) An oven dried solids determination (103-105$^{o}$C) is required. Subsample each quarter and place on a small piece of foil to be transferred to a pre-tared crucible. Refer to Standard Methods 209A pg. 93-95, of 16th (1985) edition.

(4) Combine the opposing wedges into separate I-Chem jars (i.e., two opposite wedges per jar). If more than two containers are required successively mix and quarter the opposing wedges until the sample aliquot is reduced to the size needed.

(5) Label the jars with the sample code. The jar for NCASI archives should also have an "X" added to the West Coast control number. When possible re-use original sample bottle for archives.

## V. SAMPLE STORAGE

All samples other than processed blanks are refrigerated (4$^{o}$C).

ATTACHMENT 1

AVAILABLE BLEACH PLANT INFORMATION

The following information shall be provided for each bleach line and for each type of wood processed. If both hardwood and softwood pulps are processed on the same bleach line, separate data for each type of pulp shall be provided. This provision does not require the generation of any new analytical data but rather is intended to be based on available information or estimates.

1. Current bleach plant schematic diagram (process block flow diagram) showing stages (unit operations/processes) for each bleach line and indicating the major connections and routes of flow for raw materials, chemical additives, intermediates, products, and wastewaters.

2. Typical chemical application rates and typical residual chlorine concentrations for each bleaching stage. The measurement methods for sodium hypochlorite and chlorine dioxide solution strength must be specified. All chemical application rates shall be expressed as pounds of the specific chemical per air-dried ton of brownstock pulp (e.g., lbs. $Cl_2$/ton, lbs. NaOCl/ton, lbs. $ClO_2$/ton, etc.).

3. Amount of unbleached pulp processed and bleached pulp produced in a typical operating day.

4. Typical pressure, temperature, detention time, and pH for each stage of bleaching.

5. Typical Kappa Number and Permanganate Number for brownstock pulp and for pulp at each stage of bleaching.

6. Typical brightness (GE) of pulp at each stage of bleaching.

7. Typical washing loss (lbs. $Na_2SO_4$/ton) for brownstock pulp.

8. Identify any unique process, such as oxygen delignification, that precedes pulp bleaching with chlorine.

ATTACHMENT 2

EFFLUENT, SLUDGE, AND BLEACHED PULP SAMPLING PROTOCOL

1. Five-day (5-day) composite samples of each of the following three materials shall be obtained at each mill:

   a. treated wastewater effluent prior to dilution with cooling water;

   b. combined dewatered wastewater sludge; and

   c. bleached pulp following the final stage of bleaching

   The 5-day composite samples shall be collected concurrently with individual daily composite samples. The 5-day and individual daily composite samples shall be made up of eight grab samples per day collected at approximately equally spaced time intervals. For mills which have wastewater treatment systems with retention times greater than five days, the individual daily and five-day wastewater composite samples shall be made up of at least three grab samples per day (one grab sample per eight-hour shift). The required minimum sample volume for effluents shall be in accordance with the applicable analytical protocols, and for sludge and pulp shall be one quart each. Following compositing, the individual daily composite samples shall be held, tightly sealed, in the dark at 4°C until disposition is determined, but not to exceed a period of one year.

   For plants with multiple bleach lines, discrete individual daily and 5-day composite samples of bleached pulp from each line shall be obtained. The 5 sampling days chosen shall be representative of pulp grades produced in a typical year. If both softwoods and hardwoods are bleached intermittently on the same line, sampling days shall be chosen to allow for the collection of discrete 5-day composite samples of both types of pulp.

   If primary and secondary wastewater sludges are disposed of in different fashions, then 5-day composite samples of each type of sludge must be collected.

2. Cleaning requirements for the sampling devices shall be as specified in Attachment 4 of the quality assurance project plan for the USEPA/Paper Industry Cooperative Dioxin Screening Survey (copy attached). Sample and aliquot bottles shall be cleaned according to U.S. EPA specifications for extractable organics.

3. Individual grab samples shall be obtained with dedicated, precleaned, sampling devices and deposited directly into the sample containers.

4. Samples shall be kept chilled to $4^{o}C$ and out of the light, from collection through shipment to the analytical laboratory. The 5-day composite samples shall be shipped from the mill to NCASI within twenty-four (24) hours after completion of the 5-day sampling period.

5. The following information, for each day of the 5-day sampling period, shall be obtained, recorded, and submitted to NCASI (or directly to EPA) for each mill.

   a. Wastewater effluent flow rate (24-hour total flow in gallons);

   b. Estimated wastewater sludge generation rate (wet tons/day and dry tons/day);

   c. For each bleach line, type of wood processed, brownstock pulp feed rate, and bleached pulp production rate (tons/day of air-dried pulp);

   d. For each bleach line, daily average chemical application rates of chlorine, chlorine dioxide, sodium hydroxide, sodium hypochlorite, hydrogen peroxide, and any other chemicals applied. All chemical application rates shall be expressed as pounds of the specific chemical per air-dried ton of brownstock pulp (e.g., lbs. $Cl_2$/ton, lbs. NaOCl/ton, lbs. $ClO_2$/ton.)

   e. Wastewater effluent total suspended solids (mg/l and lbs/day).

   f. Temperature and pH for each stage of bleaching, where routinely collected.

   g. Kappa Number and Permanganate Number for brownstock pulp and for pulps at each stage of bleaching, where routinely collected.

   h. Brightness of pulp for each stage of bleaching, where routinely collected.

The documentation supporting these submissions shall be retained by the mill for at least one year.

ATTACHMENT 3

WASTEWATER TREATMENT AND SLUDGE MANAGEMENT INFORMATION

Each mill subject to this agreement shall provide to EPA, through NCASI, the following information. This provision does not require the generation of any new analytical data but rather is intended to be based on available information or estimates.

1. A schematic diagram of the existing sewerage system for the mill including major wastewater sewer lines, major wastewater treatment system components, and sludge handling and dewatering facilities. To the extent available, provide daily measurements of total suspended solids in the treated process wastewater effluent (prior to dilution with noncontact cooling waters) for the period October 1986 - September 1987. The concentration of total suspended solids, daily flow rates, and daily mass discharges (lbs./day of total suspended solids) shall be provided. The estimated retention time in hours for the wastewater treatment system at a specified wastewater flow rate, typical of mill production experienced over the October 1986 - September 1987 period, shall also be provided. If the discharge is non-continuous, the mill shall provide a narrative description of typical process wastewater discharge practices.

2. For the period October 1986 - September 1987, an estimate of the monthly amounts of wastewater sludges generated (tons/day, dry weight) at the mill. Also provide a description of the current sludge disposal practice at the mill and sludge disposal practices for the past ten years.

# ATTACHMENT 4

## PULP AND PAPER INDUSTRY: CHEMICAL WOOD PULPING MILLS USING CHLORINE-BASED BLEACHING

<u>API Members</u>:

Alabama River Pulp
- Claiborne, AL

Appleton Papers, Inc.
- Roaring Springs, PA

Boise Cascade Corp.
- Jackson, AL
- DeRidder, LA
- St. Helens, OR
- Rumford, ME
- Wallula, WA
- International Falls, MN

Bowater Corp.
- Catawba, SC
- Calhoun, TN

Brunswick Pulp/Paper
- Brunswick, GA

Buckeye Cellulose (P&G)
- Perry, FL
- Oglethorpe, GA

Champion International Corp.
- Lufkin, TX
- Courtland, AL
- Quinnesec, MI
- Cantonment, FL
- Houston, TX
- Canton, NC

Chesapeake Corp.
- West Point, VA

Consolidated Papers, Inc.
- Wisconsin Rapids, WI

Federal Paper Board Co.
- Augusta, GA
- Riegelwood, NC

Finch, Pruyn & Co., Inc.
- Glens Falls, NY

Georgia-Pacific Corp.
- Bellingham, WA
- Crosset, AR
- Palatka, FL
- Woodland, ME
- Zachary, LA (Port Hudson, LA)

Gilman Paper Co.
- St. Marys, GA

Great Northern Nekoosa Corp.
- Ashdown, AR (Nekoosa Papers)
- Nekoosa, WI (Nekoosa Papers)
- New Augusta, MS (Leaf River Forest Products)
- Port Edwards, WI (Nekoosa Papers)

Gulf States Paper Corp.
    Demopolis, AL
International Paper Co.
    Bastrop, LA
    Erie, PA (Hammermill)
    Georgetown, SC
    Jay, ME
    Mobile, AL
    Moss Point, MS
    Natchez, MS
    Pine Bluff, AR
    Selma, AL (Hammermill)
    Texarkana, TX
    Ticonderoga, NY
ITT-Rayonier, Inc.
    Fernandina Beach, FL
    Hoquiam, WA
    Jesup, GA
    Port Angeles, WA
James River Corp.
    Berlin, NH
    Camas, WA
    Clatskanie, OR
    Green Bay, WI
    Old Town, ME
    St. Francesville, LA
    Butler, AL
Jefferson-Smurfit
    Brewton, AL
Longview Fibre Co.
    Longview, WA
Louisiana-Pacific Corp.
    Ketchikan, AK (Ketchikan Pulp Co.)
    Samoa, CA
Mead Corp.
    Chillicothe, OH
    Escanaba, MI
    Kingsport, TN
Penntech Papers, Inc.
    Johnsonburg, PA
Pentair, Inc.
    Park Falls, WI
Pope & Talbot, Inc.
    Halsey, OR
Potlatch Corp.
    Cloquet, MN
    Lewiston, ID
    McGeehee, AR
P.H. Glatfelter Co.
    Spring Grove, PA
Procter & Gamble Co.
    Mehoopany, PA

The following company hereby agrees to participate in the foregoing US EPA - Paper Industry Cooperative Dioxin Study (i.e., the agreement signed by Red Cavaney and Isaiah Gellman)

Company______________________________________

By___________________________________________
(Signature of Officer Authorized to Bind Company)

_____________________________ Date __________
(Signer's Typed Name)

Signer's Title:______________________________

Signer's Phone Number:_______________________

# APPENDIX B
# NCASI SAMPLING GUIDANCE

US EPA - PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

Pulp Sampling Guidance
NCASI 4/25/88

1. A one(1) quart sample size is required. Use I-CHEM Bottles No. 341-0950 (OR Equivalent).

2. Do not touch the inside of the bottle or teflon lined bottle cap. Collect all samples wearing a latex glove and discard the glove after each use if you have purchased sufficient supply. If you were unable to obtain the gloves in large quantity, they may be reused IF CARE IS TAKEN BETWEEN USES. They should be wrapped in aluminum foil(shiny side in) and dedicated to a single site for the duration of the sampling episode. We recommend that the foil packaged glove(s) be placed in a small plastic bag with the sample site identification marked on the bag. These gloves should be kept under custudy with the samples. Regardless of the procedure used, a latex glove once used for a bleached pulp SHOULD NOT be used for another sample.

3. The sample should be collected from the final stage of pulp bleaching and/or washing. The paddle normally used by the bleach plant operator to collect pulp samples can be used to withdraw a small portion of the mat. The sample should be extracted from the washer in this manner prior to putting the latex glove on and collecting the required sample aliquot. The sample should be lightly squeezed to remove loose water prior to compositing. This step will excelerate the subsequent air drying step used by the analytical laboratory.

4. You should collect a daily composite sample for EACH of FIVE(5) nearly consecutive days. You are also required to collect a composite of the five(5) day period. The daily composites will be retained by the mill while the 5 day composite will be submitted for analysis. Each "daily" composite will consist of one(1) bottle, while the five(5) day composite will be collected in AT LEAST TRIPLICATE[See Note]. Each bottle will be given a separate distinct sample ID number as directed by NCASI. The guidance that follows will be applicable to both sample types.

NOTE : Some mills will be asked to collect additional volumes of sample to assist in the development of the QA/QC plan.

5. Each daily composite will be made up of eight(8) aliquots fairly uniformly spaced during each day period and should represent steady state production. If the bleach experiences down time or a SIGNIFICANT upset, sampling should be suspended until steady state operation is re-established.

6. The volume of each sample aliquot collected can be ESTIMATED.

ICHEM Bottle No. 341-0950 has a volume of 950 cc. Hence, for the five(5) day composite, 950 cc /(5 days x 8 aliquots/day) - 25 cc/aliquot. For the "daily" composite, 950 cc / (1day x 8 aliquots/day) - 120 cc/aliquot.

7. If sampling is suspended due to process upsets, sample already collected should not be discarded. The sampler is advised to continue adding aliquots to the sample bottle until eight are collected. The sample day ends at the point. In other words, a daily composite need not be a continuous 24 hour period. If ,however, these upsets occur frequently (i.e.,more than once per day), then sampling should be suspended until the problem is defined and resolved.

8. A bleach line that swings from hardwood to softwood during a given daily period would be sampled in the manner noted in (5.). Based upon the approximate production targets for each specie, a sampling schedule can be developed that insures that eight(8) hardwood and eight(8) softwood aliquots are collected for each "daily composite." The eight aliquots will represent 24 hours of production but not necessarily a continuous 24 hour period.

9. Each mill sampler is advised to keep a log describing any unusual sampling events or process conditions not otherwise noted in the process logs. These notes should also describe how these conditions were interpreted and dealt with by the sampler.

10. Store all samples in the dark in a secured area under chain-of-custody between sampling periods. These samples do not require refrigeration for short term. However, you may want to store these samples with the sludge and effluent samples which require refrigeration.

11. Once the eight(8) aliquots are collected, the bottle cap should be tightly secured and taped with electrical tape to insure that it does not loosen in subsequent handling.

12. Place a properly signed and dated custody seal over the taped cap and store in the dark refrigerated in a secure area.

13. The 5 day composite samples should be wrapped with 1/2" bubble wrap and shipped to the analytical laboratory per NCASI direction. In all cases, one of the composites will be retained by the mill for backup purposes. The other composite sample may be required for QA/QC purposes, and mills will be advised on a case by case basis what is required. If it is not needed, it should be retained as an additional backup.

14. Bottle ID codes will be based upon the mill ID code unique to each mill. For example, Mill 45 with a single pulp line would label the bottles as follows:

| | |
|---|---|
| Day 1 Composite | M45P1 |
| Day 2 Composite | M45P2 |
| Day 3 Composite | M45P3 |
| Day 4 Composite | M45P4 |
| Day 5 Composite | M45P5 |
| 5 Day Composites | M45PC,M45PC,M45PC1 |

**Each mill will be instructed on how to number each bottle.**

US EPA - PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

Sludge Sampling Guidance
NCASI 4/25/88

1. A one(1) quart sample size is required. Use I-CHEM Bottles No. 341-0950 (OR Equivalent).

2. Do not touch the inside of the bottle or teflon lined bottle cap. Collect all solid samples wearing a latex glove and discard the glove after each use if you have purchased sufficient supply. If you were unable to obtain the gloves in large quantity, they may be reused IF CARE IS TAKEN BETWEEN USES. They should be wrapped in aluminum foil(shiny side in) and dedicated to a single site for the duration of the sampling episode. We recommend that the foil packaged glove(s) be placed in a small plastic bag with the sample site identification marked on the bag. These gloves should be kept under custudy with the samples. Regardless of the procedure used, a latex glove once used for a sludge SHOULD NOT be used for another sample.

3. The sample should be collected from the sludge dewatering device(if one is used). If the sludge is conveyed to the disposal site in a slurry form, it should be collected in that form without artifical dewatering or decanting. In these situations an extra ICHEM bottle can be used as a measuring, sampling, and/or sample transfer container. Try to keep the actual sample bottle clean.

4. You should collect a daily composite sample for EACH of FIVE(5) nearly consecutive days. You are also required to collect a composite of the five(5) day period. The daily composites will be retained by the mill while the 5 day composite will be submitted for analysis. Each "daily" composite will consist of one(1) bottle, while the five(5) day composite will be collected in AT LEAST TRIPLICATE[See Note]. Each bottle will be given a separate distinct sample ID number as directed by NCASI. The guidance that follows will be applicable to both sample types.

NOTE : Some mills will be asked to collect additional volumes to assist in developing the QA/QC plan.

5. Each daily composite ideally should be made up of eight(8) aliquots fairly uniformly spaced during each day period and should represent steady state production. If the sludge dewatering device experiences down time or a SIGNIFICANT upset, sampling should be suspended until steady state operation is re-established. If the dewatering device does not routinely operate continuously during any daily period, then the sampling schedule should be modified accordingly. The daily composite should be composed of no fewer than three aliquots spaced uniformly during the operating period. Safety concerns especially sampling sludge pond areas during evening periods may also dictate additional changes to the sampling schedule. These should be discussed on a case by case basis with NCASI.

6. The volume of each sample aliquot collected can be ESTIMATED. ICHEM Bottle No. 341-0950 has a volume of 950 cc. Hence, for the five(5) day composite, 950 cc /(5 days x 8 aliquots/day) ~ 25 cc/aliquot. For the "daily" composite, 950 cc / (1day x 8 aliquots/day) ~ 120 cc/aliquot. If sampling is suspended due to process upsets, sample already collected should not be discarded. The sampler is advised to continue adding aliquots to the sample bottle until eight are collected. The sample day ends at the point. In other words, a daily composite need not be a continuous 24 hour period. If ,however, these upsets occur frequently (i.e.,more than once per day), then sampling should be suspended until the problem is defined and resolved.

7. The eight(or fewer) aliquots will represent 24 hours of production but not necessarily a continuous 24 hour period.

8. Each mill sampler is advised to keep a log describing any unusual sampling events or process conditions not otherwise noted in the process logs. These notes should also describe how these conditions were interpreted and dealt with by the sampler.

9. Store all samples in a secured area in the dark under chain-of-custody between sampling periods. These samples require refrigeration at about 4 C.

10. Once the eight(8) (or fewer) aliquots are collected, the bottle cap should be tightly secured and taped with electrical tape to insure that it does not loosen in subsequent handling.

11. Place a properly signed and dated custody seal over the taped cap and store refrigerated in the dark in a secure area.

12. The 5 day composite samples should be wrapped with 1/2" bubble wrap and shipped to the analytical laboratory per NCASI direction. In all cases, one of the composites will be retained by the mill for backup purposes. The other composite sample may be required for QA/QC purposes, and mills will be advised on a case by case basis what is required. If it is not needed, it should be retained as an additional backup.

13. Bottle ID codes will be based upon the mill ID code unique to each mill. For example, Mill 45 with a single sludge for disposal would label the bottles as follows:

| | |
|---|---|
| Day 1 Composite | M45S1 |
| Day 2 Composite | M45S2 |
| Day 3 Composite | M45S3 |
| Day 4 Composite | M45S4 |
| Day 5 Composite | M45S5 |
| 5 Day Composites | M45SC,M45SC,M45SC1 |

Each mill will be instructed by NCASI on how to number each bottle.

US EPA - PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

Effluent Sampling Guidance
NCASI 4/25/88

1. A one(1) liter sample size is required. Use I-CHEM Bottles No. 349-1000 (OR Equivalent).

2. Do not touch the inside of the bottle or teflon lined bottle cap. Collect all liquid samples directly from the outfall structure or secondary clarifier overflow. This sampling location should coincide with your normal NPDES sampling location with the following exceptions:

a. collect samples prior to dilution with cooling water if possible
b. do not use composite sampling devices

3. The sample should be collected directly into the sample bottle if possible. A pole sampler may be constructed and used as long as a properly cleaned sample bottle is the only source of contact with the sample. An extra ICHEM Bottle No. 349-1000, for example, could be taped to a pole and used as a sampling device. A smaller volume ICHEM Bottle (349-0250, or 349 -0125) can then be used as a measuring and/or transfer device to the sample bottles. Try to keep the actual sample bottle clean and dry.

4. All sample devices should be dedicated to a site and kept under custody with the actual samples.

5. You should collect a daily composite sample for EACH of FIVE(5) nearly consecutive days. You are also required to collect a composite of the five(5) day period. The daily composites will be retained by the mill while the 5 day composite will be submitted for analysis. Each "daily" composite will consist of one(1) bottle, while the five(5) day composite will be collected in AT LEAST TRIPLICATE[See Note]. Each bottle will be given a separate distinct sample ID number as directed by NCASI. The guidance that follows will be applicable to both sample types.

NOTE : Some mills will be asked to collect additional volumes to assist in the development of the QA/QC plan.

6. For waste treatment systems with a residence time of five(5) days or less, each daily composite should be made up of eight(8) aliquots fairly uniformly spaced during each day period and should represent steady state operation of the waste treatment plant. For waste treatment systems with a residence time of greater than five(5) days, the composite samples should be made up of three(3) aliquots (one grab per operating shift).

7. If the waste treatment plant experiences down time or a SIGNIFICANT upset, sampling should be suspended until steady state or normal operation is re-established. If sampling is suspended due to process upsets, sample already collected should not be discarded. The sampler is advised to contact NCASI to discuss the nature of the upset and to receive guidance for continuing sampling. In most cases spills from pulping and bleaching will be judged sufficient to abort sampling.

8. Safety concerns especially sampling during evening periods may also dictate additional changes to the sampling schedule. These should be discussed with NCASI and will be handled on á case by case basis.

9. The volume of each sample aliquot collected can be ESTIMATED. ICHEM Bottle No. 349-1000 has a volume of 1000 cc. Hence, for the five(5) day composite, 1000 cc /(5 days x 8 aliquots/day) ~ 25 cc/aliquot. For the "daily" composite, 1000 cc / (1day x 8 aliquots/day) ~125 cc/aliquot.

10. The eight(or fewer) aliquots will represent 24 hours.

11. Each mill sampler is advised to keep a log describing any unusual sampling events or process conditions not otherwise noted in the process logs. These notes should also describe how these conditions were interpreted and dealt with by the sampler.

12. Store all samples in a secured area in the dark under chain-of-custody between sampling periods. These samples require refrigeration at about 4 C.

13. Once the eight(8) (or fewer) aliquots are collected, the bottle cap should be tightly secured and taped with electrical tape to insure that it does not loosen in subsequent handling.

14. Place a properly signed and dated custody seal over the taped cap and store refrigerated in the dark in a secure area.

15. The 5 day composite samples should be wrapped with 1/2" bubble wrap and shipped to the analytical laboratory per NCASI direction. In all cases, one of the composites will be retained by the mill for backup

purposes. The other composite sample may be required for QA/QC purposes, and mills will be advised on a case by case basis what is required. If it is not needed, it should be retained as an additional backup.

16. Bottle ID codes will be based upon the mill ID code unique to each mill. For example, Mill 45 with a single sludge for disposal would label the bottles as follows:

| | |
|---|---|
| Day 1 Composite | M45E1 |
| Day 2 Composite | M45E2 |
| Day 3 Composite | M45E3 |
| Day 4 Composite | M45E4 |
| Day 5 Composite | M45E5 |
| 5 Day Composites | M45EC,M45EC,M45EC1 |

Each mill will be instructed by NCASI on how to number each bottle.

# APPENDIX C
# NCASI DATA SHEETS FOR REPORTING PROCESS DATA

FORM A Bleach Plant Chemical Application Rates During Sampling

COMPANY : ______________________________________ MILL ID # ________

LOCATION : ______________________________________

PERSON COMPLETING FORM : ____________________ TELEPHONE : __________

SAMPLING DATE : ___________ [ One Required For EACH Day ]

WOOD SPECIE : ______________________________

* IS ANY OR ALL OF THIS INFORMATION CONFIDENTIAL ?: YES ______ NO ______ *

Bleach Plant
Chemical Application Rates [ Lbs Chemical/ ADT Brownstock ]

| STAGE | $Cl_2$ | $ClO_2$ | NaOCl | NaOH | $O_2$ | Peroxide | Other | Other |
|---|---|---|---|---|---|---|---|---|
| Brownstock | NA | NA | NA | NA | NA | NA | | |
| Oxygen Delignification | | | | | | | | |
| First Stage | | | | | | | | |
| Second Stage | | | | | | | | |
| Third Stage | | | | | | | | |
| Fourth Stage | | | | | | | | |
| Fifth Stage | | | | | | | | |
| Sixth Stage | | | | | | | | |
| Seventh Stage | | | | | | | | |

NOTE : 1. PLEASE NOTE THE UNITS REQUESTED FOR EACH ENTRY. EPA HAS REQUESTED THE DATA IN THIS FORM. IF YOU USE DIFFERENT UNITS, PLEASE CONVERT TO THOSE NOTED ABOVE IF POSSIBLE TO DO SO. OTHERWISE, PLEASE RELABEL WITH YOUR UNITS AND DESCRIBE IN THE COMMENTS SECTION.
2. ADT = AIR DRIED TONS PER DAY
3. FILL ALL UNUSED COLUMN ENTRIES WITH "NA". YOU ARE REQUIRED TO RESPOND IF THE PARAMETER IS ROUTINELY MONITORED AND REPORTED ON OPERATING LOG SHEETS.
4. IF THE "OTHER " COLUMNS ARE USED, PLEASE LIST THE CHEMICALS USED IN THE TITLE.
5. DOCUMENTATION FOR THESE SUBMISSIONS SHALL BE RETAINED BY THE MILL FOR A A PERIOD OF AT LEAST ONE YEAR.

COMMENTS : ______________________________________________

RETURN TO : Dr. Ray Whittemore
NCASI, Northeast Regional Center
Dept. of Civil Engineering
001 Anderson Hall
Tufts University
Medford, Massachusetts 02155
[ 617 - 381 - 3254 ]

FORM 8 Bleach Plant Operating Parameters During Sampling

COMPANY : ______________________________________MILL ID # ________

LOCATION : ______________________________________

PERSON COMPLETING FORM : ________________TELEPHONE :__________

SAMPLING DATE :_________[ One Required For EACH Day ]

WOOD SPECIE : ________________________________

**************************************************************************
* IS ANY OR ALL OF THIS INFORMATION CONFIDENTIAL ?: YES ______ NO ___*
**************************************************************************

Bleach Plant Operating Parameters During Sampling

| STAGE | PULP FLOW: ADT/Hour | KAPPA No. | K No. | Brightness [GE] | Temperature [F] | pH |
|---|---|---|---|---|---|---|
| Brownstock | | | | | | |
| Oxygen Delignification | | | | | | |
| First Stage | | | | | | |
| Second Stage | | | | | | |
| Third Stage | | | | | | |
| Fourth Stage | | | | | | |
| Fifth Stage | | | | | | |
| Sixth Stage | | | | | | |
| Seventh Stage | | | | | | |

NOTE : 1. PLEASE NOTE THE UNITS REQUESTED FOR EACH ENTRY. EPA HAS REQUESTED THE DATA IN THIS FORM. IF YOU USE DIFFERENT UNITS, PLEASE CONVERT TO THOSE THOSE NOTED ABOVE IF POSSIBLE TO DO SO. OTHERWISE, PLEASE RELABEL AND DESCRIBE IN THE COMMENTS SECTION.
2. ADT = AIR DRIED TONS PER DAY
3. FILL ALL UNUSED COLUMN ENTRIES WITH "NA". YOU ARE REQUIRED TO RESPOND IF THE PARAMETER IS ROUTINELY MONITORED AND REPORTED ON OPERATING LOG SHEETS.
4. IF THE "OTHER " COLUMNS ARE USED, PLEASE LIST THE CHEMICALS USED IN THE TITLE.
5. DOCUMENTATION FOR THESE SUBMISSIONS SHALL BE RETAINED BY THE MILL FOR A PERIOD OF AT LEAST ONE YEAR.

COMMENTS : ____________________________________________________________

________________________________________________________________________

________________________________________________________________________

RETURN TO : Dr. Ray Whittemore
NCASI, Northeast Regional Center
Dept. of Civil Engineering
001 Anderson Hall
Tufts University
Medford, Massachusetts 02155
[ 617 - 381 - 3254 ]

FORM C Nominal Bleach Plant Chemical Application Rates

COMPANY : ______________________________________________MILL ID # _________

LOCATION : _______________________________________________

PERSON COMPLETING FORM : ____________________TELEPHONE :___________

WOOD SPECIE : ________________________________________

* IS ANY OR ALL OF THIS INFORMATION CONFIDENTIAL ?: YES ______ NO ______ *

Bleach Plant
Nominal Chemical Application Rates [ Lbs Chemical/ ADT Brownstock ]

| STAGE | Cl2 | ClO2 | NaOCl | NaOH | O2 | Peroxide | Other | Other |
|---|---|---|---|---|---|---|---|---|
| Brownstock | NA | NA | NA | NA | NA | NA | | |
| Oxygen Delignification | | | | | | | | |
| First Stage | | | | | | | | |
| Second Stage | | | | | | | | |
| Third Stage | | | | | | | | |
| Fourth Stage | | | | | | | | |
| Fifth Stage | | | | | | | | |
| Sixth Stage | | | | | | | | |
| Seventh Stage | | | | | | | | |

NOTE : 1. PLEASE NOTE THE UNITS REQUESTED FOR EACH ENTRY. EPA HAS REQUESTED THE DATA IN THIS FORM. IF YOU USE DIFFERENT UNITS, PLEASE CONVERT TO THOSE NOTED ABOVE IF POSSIBLE TO DO SO. OTHERWISE, PLEASE RELABEL WITH YOUR UNITS AND DESCRIBE IN THE COMMENTS SECTION.
2. ADT = AIR DRIED TONS PER DAY
3. FILL ALL UNUSED COLUMN ENTRIES WITH "NA". YOU ARE REQUIRED TO RESPOND IF THE
4. PARAMETER IS ROUTINELY MONITORED AND REPORTED ON OPERATING LOG SHEETS.
IF THE "OTHER " COLUMNS ARE USED, PLEASE LIST THE CHEMICALS USED IN THE TITLE.
5. DOCUMENTATION FOR THESE SUBMISSIONS SHALL BE RETAINED FOR A PERIOD OF AT LEAST ONE YEAR.

COMMENTS : ______________________________________________________________________

RETURN TO : Dr. Ray Whittemore
NCASI, Northeast Regional Center
Dept. of Civil Engineering
001 Anderson Hall
Tufts University
Medford, Massachusetts 02155
[ 617 - 381 - 3254 ]

FORM D Nominal Bleach Plant Operating Parameters

COMPANY : ________________________________________MILL ID # _________

LOCATION : ________________________________________

PERSON COMPLETING FORM : __________________TELEPHONE :___________

WOOD SPECIE : ________________________________________

\# IS ANY OR ALL OF THIS INFORMATION CONFIDENTIAL ?: YES ______ NO ___ #

Bleach Plant
Nominal Actual Operating Parameters

| STAGE | PULP FLOW: ADT/Hour | KAPPA No. | K No. | Brightnes: [GE] | Temperature [F] | Residence: Time-Hour | pH | Washing Loss : #Na2SO4/Ton | Chlorine Residual-g/l |
|---|---|---|---|---|---|---|---|---|---|
| Brownstock | | | | NA | | | | | NA |
| Oxygen Delignification | | | | | | | | NA | NA |
| First Stage | | | | | | | | NA | |
| Second Stage | | | | | | | | NA | |
| Third Stage | | | | | | | | NA | |
| Fourth Stage | | | | | | | | NA | |
| Fifth Stage | | | | | | | | NA | |
| Sixth Stage | | | | | | | | NA | |
| Seventh Stage | | | | | | | | NA | |

NOTE : 1. PLEASE NOTE THE UNITS REQUESTED FOR EACH ENTRY. EPA HAS REQUESTED THE DATA IN THIS FORM. IF YOU USE DIFFERENT UNITS, PLEASE CONVERT THOSE NOTED ABOVE IF POSSIBLE TO DO SO. OTHERWISE, PLEASE RELABEL WITH YOUR UNITS AND DESCRIBE IN THE COMMENTS SECTION.
2. ADT = AIR DRIED TONS PER DAY
3. FILL ALL UNUSED COLUMN ENTRIES WITH "NA". YOU ARE REQUIRED TO RESPOND IF THE
4. PARAMETER IS ROUTINELY MONITORED AND REPORTED ON OPERATING LOG SHEETS. IF THE "OTHER " COLUMNS ARE USED, PLEASE LIST THE CHEMICALS USED IN THE TITLE.
5. DOCUMENTATION FOR THESE SUBMISSIONS SHALL BE RETAINED BY THE MILL FOR A PERIOD OF AT LEAST ONE YEAR.

COMMENTS : ________________________________________________________________

________________________________________________________________

________________________________________________________________

RETURN TO : Dr. Ray Whittemore
NCASI, Northeast Regional Center
Dept. of Civil Engineering
001 Anderson Hall
Tufts University
Medford, Massachusetts 02155
[ 617 - 381 - 3254 ]

FORM E Wastewater Treatment Plant Operating Data During Sampling

COMPANY : ________________________________ Mill ID # ________

LOCATION : ________________________________

PERSON COMPLETING FORM : ____________________ TELEPHONE : ________

SAMPLING DATE : ____________ [One Required For EACH Day ]

* IS ANY OR ALL OF THIS INFORMATION CONFIDENTIAL ?: YES ______ NO ______ *

Wastewater Treatment Plant
Operating Data

| Parameter | Final Effluent | Primary Sludge | Secondary Sludge | Combined Dewatered Sludge |
|---|---|---|---|---|
| Flow - MGD | | | | |
| TSS - mg/l | | | | |
| TSS - lb/day | | | | |
| Wet Tons/day | | | | |
| Dry Tons/day | | | | |

NOTE : 1. PLEASE NOTE THE UNITS REQUESTED FOR EACH ENTRY. EPA HAS REQUESTED THE UNITS IN THIS FORM. IF YOU USE DIFFERENT UNITS, PLEASE CONVERT IF POSSIBLE TO DO SO. OTHERWISE, PLEASE RELABEL WITH YOUR UNITS AND AND EXPLAIN IN THE COMMENTS SECTION.
2. THE FINAL EFFLUENT VALUES SHOULD REFLECT EFFLUENT BEFORE DILUTION WITH NON-CONTACT COOLING WATER.
3. THE SLUDGE VALUES SHOULD BE REPORTED FOR EACH SLUDGE THAT IS DISPOSED OF SEPARATELY.
4. FILL ALL UNUSED COLUMN ENTRIES WITH "NA". YOU ARE REQUIRED TO RESPOND IF THE PARAMETER IS ROUTINELY MONITORED AND REPORTED ON OPERATING LOGS.
5. DOCUMENTATION FOR THESE SUBMISSIONS SHALL BE RETAINED BY THE MILL FOR A PERIOD OF AT LEAST ONE YEAR.

COMMENTS : ________________________________

________________________________

________________________________

RETURN TO : Dr. Ray Whittemore
NCASI, Northeast Regional Center
Dept. of Civil Engineering
001 Anderson Hall
Tufts University
Medford, Massachusetts 02155
[ 617 - 381 - 3254 ]

# APPENDIX D
# SUMMARY OF ALL 2378-TCDD AND 2378-TCDF ANALYTICAL DATA

| MILL NAME | MILL LOCATION | PULP TCDD (PPT) | PULP TCDF (PPT) | EFFLUENT TCDD (PPQ) | EFFLUENT TCDF (PPQ) | SLUDGE TCDD (PPT) | SLUDGE TCDF (PPT) |
|---|---|---|---|---|---|---|---|
| Alabama River | Claiborne, Al | 3.9 | 97 | 41 | 250 | 81 | 373 |
| Alabama River | | 43 | 120 | | | | |
| Appleton Papers | Roaring Springs, PA | 1 | 21 | ND(11) | 18 | 5 | 113 |
| Boise Cascade | Jackson, Al | 11 | 104 | 95 | 540 | 18 | 147 |
| Boise Cascade | DeRidder, LA | 5.3 | 8.7 | 9.2 | 44 | 0.28 | 0.44 |
| Boise Cascade | St. Helens, OR | 4.2 | 12 | 22 | 100 | 4.2 | 25 |
| Boise Cascade | | 6.5 | 18 | | | | |
| Boise Cascade | Rumford, ME | 17 | 111 | 120 | 570 | 105 | 674 |
| Boise Cascade | | 116 | 800 | | | | |
| Boise Cascade | Wallula, WA | 56 | 1380 | 360 | 7500 | 70 | 1490 |
| Bowater Carolina | Catawba, SC | 2.1 | 3.3 | 24 | 42 | 0.62 | 0.88 |
| Bowater Southern | Calhoun, TN | 7.7 | 53 | ND(6.8) | ND(5.5) | 4.5 | 14 |
| Brunswick P/P | Brunswick, GA | 1.9 | 3.5 | 30 | 68 | 32 | 62 |
| Brunswick P/P | | 3.6 | 4.3 | | | | |
| Brunswick P/P | | 6.3 | 8 | | | | |
| Brunswick P/P | | 8.3 | 12 | | | | |
| Buckeye Cellulose | Perry, FL | 0.5 | 0.7 | 27 | 80 | 12 | 40 |
| Buckeye Cellulose | | ND(0.8) | 2.5 | | | | |
| Buckeye Cellulose | Oglethorpe, GA | ND(0.5) | ND(0.9) | ND(12) | 26 | 2.6 | 3 |
| Champion Inter'l | Courtland, AL | 23 | 102 | 77 | 340 | 215 | 923 |
| Champion Inter'l | | 3.5 | 7.6 | | | | |
| Champion Inter'l | Quinnesec, MI | 7.7 | 50 | 9 | 66 | 95 | 735 |
| Champion Inter'l | Cantonment, FL | 2 | 0.9 | ND(11) | 38 | 14 | 21 |
| Champion Inter'l | | ND(1) | ND(0.07) | | | | |

| MILL NAME | MILL LOCATION | PULP TCDD (PPT) | PULP TCDF (PPT) | EFFLUENT TCDD (PPQ) | EFFLUENT TCDF (PPQ) | SLUDGE TCDD (PPT) | SLUDGE TCDF (PPT) |
|---|---|---|---|---|---|---|---|
| Champion Inter'l | Houston, TX | 4.9 | 6.8 | ND(5.5) | 11, ND(5.8) | 106 | 144 |
| Champion Inter'l | Canton, NC | 6 | 9.9 | 15 | 7.2 | 172 | 260 |
| Champion Inter'l | | 5.8 | 10 | | | | |
| Champion Inter'l | | 6.5 | 11 | | | | |
| Champion Inter'l | | 17 | 27 | | | | |
| Chesapeake Corp. | West Point, VA | 8.3 | 14 | 16 | 96 | 14 | 47 |
| CCA | Brewton, AL | 2.3 | 4.5 | 6.5 | ND(10) | 16 | 34 |
| Flambeau Paper | Park Falls, WI | ND(0.5) | ND(0.9) | ND(5.4) | 4.8 | 10.2 | 81.5 |
| Federal Paperboard | Riegelwood, NC | 4 | 3.2 | 28, Anal. Diff | 61, Anal. Diff | 3.8 | 5.2 |
| Federal Paperboard | | 4.3 | 4.7 | ND(11), ND(21) | 31, 31 | | |
| Federal Paperboard | | 3.2 | 1.3 | | | | |
| Federal Paperboard | Augusta, GA | 2.4 | 7.9 | 16 | 47 | 0.68 | 1.4 |
| Federal Paperboard | | 4.9 | 15 | | | | |
| Federal Paperboard | | 7.9 | 19 | | | | |
| Finch Pryun | Glen Falls, NY | ND(0.3) | ND(0.3) | ND(7.9) | ND(2.9) | 1.2 | 7.4 |
| Georgia Pacific | Bellingham, WA | 3.5 | 409 | ND(5.3) | 840 | 19 | 584 |
| Georgia Pacific | Crossett, AR | 7.7 | 89 | 96 | 370 | 168 | 1680 |
| Georgia Pacific | | 19 | 308 | | | 0.19 | 0.71 |
| Georgia Pacific | | 6 | 59 | | | | |
| Georgia Pacific | Palatka, FL | ND(0.5) | ND(0.9) | 16 | 38 | 0.092 | 0.4 |
| Georgia Pacific | | ND(0.5) | 2.4 | | | | |
| Georgia Pacific | Woodland, ME | ND(0.4) | 0.9 | 6.8 | 25 | ND(1.9) | 7.3 |
| Georgia Pacific | Zachary, LA | 16 | 539 | 175 | 3000 | 17 | 421 |
| Georgia Pacific | | 5.2 | 78 | | | | |
| Georgia Pacific | | 27 | 632 | | | | |

| MILL NAME | MILL LOCATION | PULP TCDD (PPT) | PULP TCDF (PPT) | EFFLUENT TCDD (PPQ) | EFFLUENT TCDF (PPQ) | SLUDGE TCDD (PPT) | SLUDGE TCDF (PPT) |
|---|---|---|---|---|---|---|---|
| PH Glatfelter | Spring Grove, PA | 3.6 | 12 | ND(8.4) | 26 | 93 | 238 |
| PH Glatfelter | | 0.4 | 2 | | | | |
| Procter & Gamble | Mehoopany, PA | 2 | 1.1 | ND(9.7) | 2.8 | ND(0.3) | 0.7 |
| Scott Paper Co. | Everett, WA | ND(0.3) | ND(0.1) | ND(7.5) | 29 | 14 | 72 |
| Scott Paper Co. | | | | ND(8.3) | ND(2.6) | | |
| Scott Paper Co. | Mobile, AL | 0.6 | 0.8 | 14 | 19 | 9.5 | 18 |
| Scott Paper Co. | | 2 | 3.2 | | | | |
| Scott Paper Co. | Skowhegan, ME | 1.9 | 10 | 16 | 63 | 33 | 106 |
| Scott Paper Co. | | 8.5 | 37 | | | 6.9 | 29 |
| Scott Paper Co. | | | | | | 67 | 330 |
| Scott Paper Co. | Muskegon, MI | ND(0.3) | 1.2 | ND(8.4) | 42 | | |
| Scott Paper Co. | Westbrook, ME | 8.1 | 30 | 6.3 | 12 | 13 | 55 |
| Scott Paper Co. | | 4.2 | 16 | | | | |
| Simpson Paper Co. | Anderson, CA | 49 | 2620 | 250 | 8400 | 278 | 6740 |
| Simpson Paper Co. | Fairhaven, CA | 20 | 106 | 100 | 660 | | |
| Simpson Paper Co. | Pasadena, TX | 14 | 48 | 250 | 730 | | |
| Simpson Paper Co. | | 4.5 | 11 | | | | |
| Simpson Paper Co. | Tacoma, WA | 12 | 38 | Anal. Diff. | 26 | 39 | 100 |
| | | | | 17 | 100 | 30 | 176 |
| St. Joe Forest | St. Joe, FL | 2.2 | 5.7 | 21 | 60 | | |
| Stone Container | Missoula, MT | 4.1 | 13 | 3.1 | ND(7.7) | 0.055 | 0.15 |
| Stone Container | Panama City, FL | ND(0.1) | 6.6 | ND(8.4) | 7.9 | 3.6 | 16 |
| Stone Container | Snowflake, AZ | ND(0.7) | 1.3 | 5.5 | 39 | | |

| MILL NAME | MILL LOCATION | PULP TCDD (PPT) | PULP TCDF (PPT) | EFFLUENT TCDD (PPQ) | EFFLUENT TCDF (PPQ) | SLUDGE TCDD (PPT) | SLUDGE TCDF (PPT) |
|---|---|---|---|---|---|---|---|
| Temple-Eastex | Evadale, TX | 3.1 | 6.3 | 88 | 100 | 16 | 49 |
| Temple-Eastex | | 1.9 | 9.6 | | | | |
| Temple-Eastex | | 7.8 | 22 | | | | |
| Temple-Eastex | | 4.1 | 13 | | | | |
| Union Camp | Eastover, SC | ND(0.4) | 1.3 | 20 | 53 | 6.9 | 13 |
| Union Camp | | 2.4 | 5.6 | | | | |
| Union Camp | Franklin, VA | 1.1 | 2.1 | 68 | 71 | 3.6 | 6 |
| Union Camp | | 5.4 | 6.9 | | | | |
| Union Camp | | 3.2 | 3.6 | | | | |
| Union Camp | | 3.8 | 4.2 | | | | |
| Westvaco | Covington, VA | 13 | 105 | 180 | 520 | 119 | 799 |
| Westvaco | | 6.2 | 49 | | | | |
| Westvaco | | 5.9 | 19 | | | | |
| Westvaco | Luke, MD | 29 | 157 | 16 | 49 | 80 | 471 |
| Westvaco | Wickliffe, KY | 2.1 | 25 | 35 | 150 | 9.4 | 46 |
| Westvaco | | 12 | 55 | | | | |
| Weyerhaeuser | Cosmopolis, WA | ND(0.3) | 3.1 | 9.7 | 400 | 12 | 61 |
| Weyerhaeuser | | ND(1) | 6.3 | | | | |
| Weyerhaeuser | Everett, WA | 3.4 | 16 | 33 | 260 | | |
| Weyerhaeuser | | 5.2 | 20 | | | | |
| Weyerhaeuser | Longview, WA | 1.7 | 2.8 | 10 | 37 | 35 | 89 |
| Weyerhaeuser | | 7.7 | 20 | | | | |
| Weyerhaeuser | | 1.7 | 9.4 | | | | |
| Weyerhaeuser | New Bern, NC | 7.5 | 45 | 44 | 180 | 293 | 1760 |
| Weyerhaeuser | Plymouth, NC | 10 | 82 | 320 | 4000 | 1390 | 17100 |
| Weyerhaeuser | | 14 | 222 | | | | |
| Weyerhaeuser | | 33 | 318 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Weyerhaeuser | Rothchild, WI | 15 | 26 | 12 | 18 | 58 | 150 |
| Willamette Ind. | Hawesville, KY | ND(0.3) | 1.1 | ND(11) | ND(8) | 0.083 | 0.38 |
| Willamette Ind. | | ND(0.5) | 1.9 | | | 0.052 | 0.21 |
| Alaska Pulp Corp. | Sitka, AK | ND(0.7) | 1.4 | ND(7.7) | 32 | 4.7 | 42 |
| Badger Paper | Peshtigo, WI | 4.4 | 323 | 9.8, ND(6.4) | 225 | 0.036 | 1.8 |
| Badger Paper | | | | 4.5, ND(5.3) | 120 | | |
| Kimberly-Clark | Coosa Pines, AL | ND(0.3) | 1 | 35 | 74 | 3.8 | 9.2 |
| Kimberly-Clark | | 4.1 | 7.3 | | | | |
| Kimberly-Clark | | 11 | 38 | | | | |
| Kimberly-Clark | | 2.6 | 3.3 | | | | |
| Lincoln P&Paper | Lincoln, ME | 16 | 94 | 32 | 130 | 48 | 223 |
| Wausau Papers | Wausau, WI | ND(0.4) | 9.9 | ND(4.5) | 14, ND(2) | 3.65 | 62 |
| Gilman Paper Co. | St. Mary's, FL | 2.8 | 6.8 | ND(6.5) | 17 | 0.22 | 0.6 |
| Gilman Paper Co. | | 3.7 | 12 | | | | |
| Gulf States Paper | Demopolis, AL | 5.2 | 20 | 38 | 110 | 44 | 107 |
| Hammermill Papers | Erie, PA | 6.4 | 22 | 24 | 68 | 0.9 | 3.1 |
| Hammermill Papers | Selma, AL | 4.7 | 22 | 81 | 310 | 0.68 | 2.9 |
| Hammermill Papers | | 2.1 | 21 | | | | |
| IPCo. | Bastrop, LA | 6.3 | 42 | 330 | 1600 | 140 | 677 |
| IPCo. | | 5.1 | 22 | | | | |
| IPCo. | Georgetown, SC | 1.9 | 7.7 | 640 | 1600 | 62 | 161 |
| IPCo. | | 17 | 55 | | | | |
| IPCo. | | 9.2 | 38 | | | | |
| IPCo. | Mobile, AL | 21 | 106 | 100 | 850, 490 | 108 | 617 |
| James River Corp. | | 12 | 152 | | | | |
| James River Corp. | Green Bay, WI | ND(0.8) | 7.1 | 19 | 72 | 35 | 250 |
| James River Corp. | | | | ND(8.5) | 2.9 | | |

| MILL NAME | MILL LOCATION | PULP TCDD (PPT) | PULP TCDF (PPT) | EFFLUENT TCDD (PPQ) | EFFLUENT TCDF (PPQ) | SLUDGE TCDD (PPT) | SLUDGE TCDF (PPT) |
|---|---|---|---|---|---|---|---|
| James River Corp. | Old Town, ME | .13 | 51 | 39 | 130 | 12 | 34 |
| James River Corp. | St. Francisville, LA | 6.4 | 19 | 82 | 320 | 96 | 243 |
| James River Corp. | | 4.9 | 15 | | | | |
| James River Corp. | Naheola, AL | 3.7 | 30 | 23 | 72 | 0.33 | 1.1 |
| James River Corp. | | 1.2 | 1.4 | | | | |
| James River Corp. | | 3.3 | 19 | | | | |
| Leaf River | New Augusta, MS | 3.8 | 7.7 | 200 | 410 | 756 | 1300 |
| Leaf River | | 15 | 35 | | | | |
| Longview Fibre | Longview, WA | 4.4 | 28 | ND(4.6) | 57 | 69 | 437 |
| Longview Fibre | | 4.7 | 26 | | | | |
| Ketchikan Pulp | Ketchikan, AK | ND(0.3) | ND(0.3) | ND(6.7) | ND(5.3) | 0.4 | 2 |
| Ketchikan Pulp | | | | 15 | 7.2 | | |
| Louisiana Pacific | Samoa, CA | 8.4 | 55 | 67 | 320,170 | | |
| Mead Paper | Escanaba, MI | 15 | 39 | ND(17) | 50.8 | 125 | 574 |
| Mead Paper | | 25 | 116 | | | | |
| Mead Paper | Kingsport, TN | 1.5 | 26 | 6 | 44 | ND(3) | 25 |
| Nekoosa Papers | Ashdown, AR | 5.5 | 12 | 41 | 94 | 13 | 30 |
| Nekoosa Papers | | 2.8 | 27 | | | | |
| Nekoosa Papers | Nekoosa, WI | 22 | 283 | 40 | 320 | 109 | 1300 |
| Nekoosa Papers | Port Edwards, WI | ND(0.4) | 4.1 | | | | |
| Penntech Papers | Johnsonburg, PA | 3.1 | 38 | ND(6.8) | 14 | | |
| Penntech Papers | | | | 9.7 | 65 | | |
| Pope&Talbot | Haslsey, OR | 10 | 41 | 30 | 82 | 31 | 106 |
| Pope&Talbot | | | | | | | |
| Potlatch Corp. | Cloquet, MN | 1.1 | 4.6 | 24 | 46 | 5 | 25 |

# APPENDIX E
# FULL CONGENER DATA WITH QA/QC SUMMARY

Villiam J. Gillespie
Program Director
Water Quality
(212) 532-9001

August 2, 1989

Mr. Thomas P. O'Farrell (WH-552)
Office of Water
U.S. E.P.A.
401 M St. S.W.
Washington, D.C. 20460

Dear Mr. O'Farrell:

Enclosed are the results of 'full congener' dioxin and furan analyses as called for under Section 3.6 (c) of the Industry/EPA Cooperative Study Agreement. To the extent possible the data are presented in a format comparable to our standard reporting format under the Cooperative Study Agreement.

You will note that we have analyzed all three vectors for nine mills (as per the agreement) and carried out duplicate analyses at one mill for each vector.

If you have any questions concerning this data, please feel free to contact me.

Very truly yours,

William J. Gillespie /dch

William J. Gillespie
Program Director - Water Quality

cc: Matt Van Hook

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | | MILL B | | | MILL C | | | MILL D | | | MILL D DUPLICATE | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Sludge | | | Combined sludge | | | Dewatered sludge | | | Sludge | | | Sludge | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | |
| Analytes | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 63 | 0.81 | | 180 | 0.78 | | 6.8 | 0.89 | | 88 | 0.74 | | 92 | 0.75 | |
| non-2,3,7,8-TCDD | ND(1.9)a | NA | | 74 | NA | | D(1.5)a | NA | | ND(1.5)a | NA | | ND(1.5)a | NA | |
| 13C-TCDD | | | 88 | | | 75 | | | 70 | | | 68 | | | 63 |
| 1,2,3,7,8-PeCDD | ND(4.7) | NA | | ND(7.8)a | NA | | ND(2.2) | NA | | ND(2.5) | NA | | ND(3.1) | NA | |
| non-2,3,7,8 sub PeCDD | 10 | NA | | ND(7.8) | NA | | ND(2.2) | NA | | ND(2.5) | NA | | ND(3.1) | NA | |
| 13C-PeCDD | | | 69 | | | 93 | | | 56 | | | 59 | | | 78 |
| 1,2,3,4,7,8-HxCDD | ND(2.4) | NA | | ND(3.5) | NA | | ND(1.7) | NA | | ND(4.0) | NA | | ND(4.8) | NA | |
| 1,2,3,6,7,8-HxCDD | ND(2.4) | NA | | ND(3.4) | NA | | ND(1.7) | NA | | ND(2.7) | NA | | ND(4.8) | NA | |
| 1,2,3,7,8,9-HxCDD | ND(3.2) | NA | | ND(2.1) | NA | | ND(1.7) | NA | | ND(4.0) | NA | | ND(4.8) | NA | |
| non-2,3,7,8 sub HxCDD | 8.7 | NA | | 11 | NA | | 4.2 | NA | | 8.0 | NA | | 9.9 | NA | |
| 13C-HxCDD | | | 91 | | | 85 | | | 75 | | | 81 | | | 77 |
| 1,2,3,4,6,7,8-HpCDD | 18 | 1.11 | | 35 | 1.14 | | 21 | 0.99 | | 34 | 1.06 | | 35 | 0.99 | |
| non-2,3,7,8 sub HpCDD | 18 | NA | | 33 | NA | | 18 | NA | | 42 | NA | | 43 | NA | |
| 13C-HpCDD | | | 116 | | | 100 | | | 95 | | | 110 | | | 81 |
| OCDD | 263 | 0.88 | | 677 | 0.90 | | 335 | 0.86 | | 719 | 0.88 | | 687 | 0.88 | |
| 13C-OCDD | | | 83 | | | 75 | | | 74 | | | 88 | | | 61 |
| 2,3,7,8-TCDF | 273 | 0.79 | | 328 | 0.79 | | 13 | 0.76 | | 233 | 0.75 | | 233 | 0.77 | |
| non-2,3,7,8-TCDF | 547 | NA | | 730 | NA | | 37 | NA | | 412 | NA | | 423 | NA | |
| 13C-TCDF | | | 101 | | | 76 | | | 80 | | | 76 | | | 62 |
| 1,2,3,7,8-PeCDF | 7.8 | 1.40 | | 12 | 1.44 | | ND(1.2) | NA | | 4.9 | 1.48 | | 5.5 | 1.32 | |
| 2,3,4,7,8-PeCDF | 4.7 | 1.34 | | 7.0 | 1.38 | | ND(0.9) | NA | | 3.1 | 1.35 | | 3.9 | 1.45 | |
| non-2,3,7,8 sub PeCDF | 16 | NA | | 28 | NA | | ND(2.5) | NA | | 14 | NA | | 12 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(1.7) | NA | | 4.8 | 1.26 | | ND(0.9) | NA | | ND(1.9) | NA | | ND(2.6) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(1.7) | NA | | ND(1.7) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(1.8) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(1.7) | NA | | ND(1.9) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(2.6) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(1.7) | NA | | ND(1.9) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(2.6) | NA | |
| non-2,3,7,8 sub HxCDF | 2.0 | NA | | ND(1.9) | NA | | ND(0.9) | NA | | 5.2 | NA | | 4.3 | NA | |
| 1,2,3,4,6,7,8-HpCDF | 3.5 | 1.05 | | 5.5 | 1.09 | | ND(3.6) | NA | | ND(4.5) | NA | | 6.0 | 1.15 | |
| 1,2,3,4,7,8,9-HpCDF | ND(1.2) | NA | | ND(1.4) | NA | | ND(3.6) | NA | | ND(4.5) | NA | | ND(1.0) | NA | |
| non-2,3,7,8 sub HpCDF | ND(1.2) | NA | | 5.7 | NA | | 4.8 | NA | | 5.9 | NA | | ND(1.0) | NA | |
| OCDF | 14 | 0.87 | | 13 | 0.95 | | 14 | 0.76 | | 22 | 0.84 | | 23 | 0.85 | |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

b--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in [] is the internal standard recovery.

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | | MILL B | | | MILL C | | | MILL D | | | MILL D DUPLICATE | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Sludge | | | Combined sludge | | | Dewatered sludge | | | Sludge | | | Sludge | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | | 06/19/89 | | |
| Analytes | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 63 | 0.81 | | 180 | 0.78 | | 6.8 | 0.89 | | 88 | 0.74 | | 92 | 0.75 | |
| non-2,3,7,8-TCDD | ND(1.9)a | NA | | 74 | NA | | D(1.5)a | NA | | ND(1.5)a | NA | | ND(1.5)a | NA | |
| 13C-TCDD | | | 88 | | | 75 | | | 70 | | | 68 | | | 63 |
| 1,2,3,7,8-PeCDD | ND(4.7) | NA | | ND(7.8)a | NA | | ND(2.2) | NA | | ND(2.5) | NA | | ND(3.1) | NA | |
| non-2,3,7,8 sub PeCDD | 10 | NA | | ND(7.8) | NA | | ND(2.2) | NA | | ND(2.5) | NA | | ND(3.1) | NA | |
| 13C-PeCDD | | | 69 | | | 93 | | | 56 | | | 59 | | | 78 |
| 1,2,3,4,7,8-HxCDD | ND(2.4) | NA | | ND(3.5) | NA | | ND(1.7) | NA | | ND(4.0) | NA | | ND(4.8) | NA | |
| 1,2,3,6,7,8-HxCDD | ND(2.4) | NA | | ND(3.4) | NA | | ND(1.7) | NA | | ND(2.7) | NA | | ND(4.8) | NA | |
| 1,2,3,7,8,9-HxCDD | ND(3.2) | NA | | ND(2.1) | NA | | ND(1.7) | NA | | ND(4.0) | NA | | ND(4.8) | NA | |
| non-2,3,7,8 sub HxCDD | 8.7 | NA | | 11 | NA | | 4.2 | NA | | 8.0 | NA | | 9.9 | NA | |
| 13C-HxCDD | | | 91 | | | 85 | | | 75 | | | 81 | | | 77 |
| 1,2,3,4,6,7,8-HpCDD | 18 | 1.11 | | 35 | 1.14 | | 21 | 0.99 | | 34 | 1.06 | | 35 | 0.99 | |
| non-2,3,7,8 sub HpCDD | 18 | NA | | 33 | NA | | 18 | NA | | 42 | NA | | 43 | NA | |
| 13C-HpCDD | | | 116 | | | 100 | | | 95 | | | 110 | | | 81 |
| OCDD | 263 | 0.88 | | 677 | 0.90 | | 335 | 0.86 | | 719 | 0.88 | | 687 | 0.88 | |
| 13C-OCDD | | | 83 | | | 75 | | | 74 | | | 88 | | | 61 |
| 2,3,7,8-TCDF | 273 | 0.79 | | 328 | 0.79 | | 13 | 0.76 | | 233 | 0.75 | | 233 | 0.77 | |
| non-2,3,7,8-TCDF | 547 | NA | | 730 | NA | | 37 | NA | | 412 | NA | | 423 | NA | |
| 13C-TCDF | | | 101 | | | 76 | | | 80 | | | 76 | | | 62 |
| 1,2,3,7,8-PeCDF | 7.8 | 1.40 | | 12 | 1.44 | | ND(1.2) | NA | | 4.9 | 1.48 | | 5.5 | 1.32 | |
| 2,3,4,7,8-PeCDF | 4.7 | 1.34 | | 7.0 | 1.38 | | ND(0.9) | NA | | 3.1 | 1.35 | | 3.9 | 1.45 | |
| non-2,3,7,8 sub PeCDF | 16 | NA | | 28 | NA | | ND(2.5) | NA | | 14 | NA | | 12 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(1.7) | NA | | 4.8 | 1.26 | | ND(0.9) | NA | | ND(1.9) | NA | | ND(2.6) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(1.7) | NA | | ND(1.7) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(1.8) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(1.7) | NA | | ND(1.9) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(2.6) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(1.7) | NA | | ND(1.9) | NA | | ND(0.9) | NA | | ND(1.2) | NA | | ND(2.6) | NA | |
| non-2,3,7,8 sub HxCDF | 2.0 | NA | | ND(1.9) | NA | | ND(0.9) | NA | | 5.2 | NA | | 4.3 | NA | |
| 1,2,3,4,6,7,8-HpCDF | 3.5 | 1.05 | | 5.5 | 1.09 | | ND(3.6) | NA | | ND(4.5) | NA | | 6.0 | 1.15 | |
| 1,2,3,4,7,8,9-HpCDF | ND(1.2) | NA | | ND(1.4) | NA | | ND(3.6) | NA | | ND(4.5) | NA | | ND(1.0) | NA | |
| non-2,3,7,8 sub HpCDF | ND(1.2) | NA | | 5.7 | NA | | 4.8 | NA | | 5.9 | NA | | ND(1.0) | NA | |
| OCDF | 14 | 0.87 | | 13 | 0.95 | | 14 | 0.76 | | 22 | 0.84 | | 23 | 0.85 | |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

b--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in [] is the internal standard recovery.

MILL E
Sludge
CAL ANALYTICAL
06/19/89

MILL F
Combined dewatered sludge
CAL ANALYTICAL
06/19/89

MILL G
Dewatered primary sludge
CAL ANALYTICAL
06/19/89

MILL H
Sludge
CAL ANALYTICAL
06/19/89

MILL I
Primary Sludge
CAL ANALYTICAL
06/19/89

| MILL E CONC. ODS (ppt) | MILL E ION RATIO | MILL E PERCENT INTERNAL STANDARD RECOVERY | MILL F CONC. ODS (ppt) | MILL F ION RATIO | MILL F PERCENT INTERNAL STANDARD RECOVERY | MILL G CONC. ODS (ppt) | MILL G ION RATIO | MILL G PERCENT INTERNAL STANDARD RECOVERY | MILL H CONC. ODS (ppt) | MILL H ION RATIO | MILL H PERCENT INTERNAL STANDARD RECOVERY | MILL I CONC. ODS (ppt) | MILL I ION RATIO | MILL I PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 147 | 0.88 | | 24 | 0.81 | | ND(6.3)a | NA | | 116 | 0.77 | | 14 | 0.79 | |
| D(1.2)a | NA | | 837 | NA | | ND(6.3) | NA | | ND(1.1)a | NA | | ND(1.1)a | NA | |
| | | 85 | | | 77 | | | 74 | | | 62 | | | 84 |
| ND(7.2) | NA | | 28 | 1.58 | | ND(1.4) | NA | | ND(2.9) | NA | | ND(1.6) | NA | |
| 7.2 | NA | | 1280 | NA | | ND(1.4) | NA | | ND(2.9) | NA | | ND(1.6) | NA | |
| | | 71 | | | 62 | | | 57 | | | 51 | | | 60 |
| ND(3.7) | NA | | 40 | 1.26 | | ND(3.5) | NA | | ND(1.5) | NA | | ND(3.1) | NA | |
| ND(3.2) | NA | | 95 | 1.43 | | ND(5.4) | NA | | ND(8.6) | NA | | ND(3.1) | NA | |
| ND(4.3) | NA | | 80 | 1.31 | | ND(3.9) | NA | | ND(5.3) | NA | | ND(3.1) | NA | |
| 14 | NA | | 2180 | NA | | 38 | NA | | 64 | NA | | ND(3.1) | NA | |
| | | 88 | | | 81 | | | 79 | | | 67 | | | 77 |
| 80 | 1.00 | | 490 | 1.05 | | 136 | 1.06 | | 37 | 1.08 | | 39 | 1.11 | |
| 119 | NA | | 447 | NA | | 115 | NA | | 35 | NA | | 32 | NA | |
| | | 110 | | | 102 | | | 94 | | | 78 | | | 62 |
| 1780 | 0.89 | | 1090 | 0.88 | | 1460 | 0.89 | | 399 | 0.89 | | 698[19%]b | 0.84 | |
| | | 91 | | | 82 | | | 73 | | | 53 | | | 19 |
| 1150 | 0.78 | | 69 | 0.68 | | 27 | 0.85 | | 536 | 0.77 | | 29 | 0.80 | |
| 2310 | NA | | 650 | NA | | 48 | NA | | 830 | NA | | 109 | NA | |
| | | 85 | | | 94 | | | 88 | | | 58 | | | 105 |
| 22 | 1.49 | | 21 | 1.44 | | ND(1.2) | NA | | 6.2 | 1.37 | | ND(1.2) | NA | |
| 18 | 1.68 | | 38 | 1.56 | | ND(1.6) | NA | | 5.3 | 1.41 | | ND(1.3) | NA | |
| 41 | NA | | 268 | NA | | ND(2.0) | NA | | 6.4 | NA | | 5.5 | NA | |
| ND(2.5) | NA | | 31 | 1.30 | | ND(3.0) | NA | | ND(4.0) | NA | | ND(1.2) | NA | |
| ND(1.4) | NA | | 33 | 1.25 | | ND(2.3) | NA | | ND(1.2) | NA | | ND(1.2) | NA | |
| ND(2.0) | NA | | 34 | 1.07 | | ND(3.0) | NA | | ND(1.2) | NA | | ND(1.2) | NA | |
| ND(2.2) | NA | | ND(4.0)a | NA | | ND(3.0) | NA | | ND(1.2) | NA | | ND(1.2) | NA | |
| 19 | NA | | 219 | NA | | 21 | NA | | 19 | NA | | 3.2 | NA | |
| 7.9 | 1.12 | | 70 | 1.06 | | 17 | 1.10 | | 54 | 1.07 | | 6.6 | 1.04 | |
| ND(1.4) | NA | | 10 | 1.15 | | ND(1.6) | NA | | ND(1.4) | NA | | ND(4.3) | NA | |
| 17 | NA | | 63 | NA | | 41 | NA | | 41 | NA | | 12.7 | NA | |
| 35 | 0.84 | | 60 | 0.93 | | 84 | 0.86 | | 168 | 0.81 | | ND(54) | NA | |

Quality Assurance Data Summary
Precision Data
Laboratory Duplicate

| | |
|---|---|
| Mill Code | MILL D |
| Matrix | Sludge |
| Laboratory | CAL ANALYTICAL |
| Laboratory Report Date | 06/19/89 |

| | #1 | | | #2 | | | |
|---|---|---|---|---|---|---|---|
| | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | Relative Percent Difference |
| 2,3,7,8-TCDD | 88 | 0.74 | | 92 | 0.75 | | 4 |
| non-2,3,7,8-TCDD | ND(1.5)a | NA | | ND(1.5)a | NA | | NA |
| | | | 68 | | | 63 | |
| 1,2,3,7,8-PeCDD | ND(2.5) | NA | | ND(3.1) | NA | | NA |
| non-2,3,7,8 sub PeCDD | ND(2.5) | NA | | ND(3.1) | NA | | NA |
| | | | 59 | | | 78 | |
| 1,2,3,4,7,8-HxCDD | ND(4.0) | NA | | ND(4.8) | NA | | NA |
| 1,2,3,6,7,8-HxCDD | ND(2.7) | NA | | ND(4.8) | NA | | NA |
| 1,2,3,7,8,9-HxCDD | ND(4.0) | NA | | ND(4.8) | NA | | NA |
| non-2,3,7,8 sub HxCDD | 8.0 | NA | | 9.9 | NA | | 21 |
| | | | 81 | | | 77 | |
| 1,2,3,4,6,7,8-HpCDD | 34 | 1.06 | | 35 | 0.99 | | 3 |
| non-2,3,7,8 sub HpCDD | 42 | NA | | 43 | NA | | 2 |
| | | | 110 | | | 81 | |
| OCDD | 719 | 0.88 | | 687 | 0.88 | | 5 |
| | | | 88 | | | 61 | |
| 2,3,7,8-TCDF | 233 | 0.75 | | 233 | 0.77 | | 0 |
| non-2,3,7,8-TCDF | 412 | NA | | 423 | NA | | 3 |
| | | | 76 | | | 62 | |
| 1,2,3,7,8-PeCDF | 4.9 | 1.48 | | 5.5 | 1.32 | | 12 |
| 2,3,4,7,8-PeCDF | 3.1 | 1.35 | | 3.9 | 1.45 | | 23 |
| non-2,3,7,8 sub PeCDF | 14 | NA | | 12 | NA | | 15 |
| 1,2,3,4,7,8-HxCDF | ND(1.9) | NA | | ND(2.6) | NA | | NA |
| 1,2,3,6,7,8-HxCDF | ND(1.2) | NA | | ND(1.8) | NA | | NA |
| 2,3,4,6,7,8-HxCDF | ND(1.2) | NA | | ND(2.6) | NA | | NA |
| 1,2,3,7,8,9-HxCDF | ND(1.2) | NA | | ND(2.6) | NA | | NA |
| non-2,3,7,8 sub HxCDF | 5.2 | NA | | 4.3 | NA | | 19 |
| 1,2,3,4,6,7,8-HpCDF | ND(4.5) | NA | | 6.0 | 1.15 | | NA |
| 1,2,3,4,7,8,9-HpCDF | ND(4.5) | NA | | ND(1.0) | NA | | NA |
| non-2,3,7,8 sub HpCDF | 5.9 | NA | | ND(1.0) | NA | | NA |
| OCDF | 22 | 0.84 | | 23 | 0.85 | | 4 |

a--ND designates "not detected" above the minimum detectable concentration.
The number in parenthesis is the detection limit.

Quality Assurance Data Summary
Recovery Data

| | |
|---|---|
| Mill Code | MILL D |
| Matrix | Sludge |
| Laboratory | CAL ANALYTICAL |
| Laboratory Report Date | 06/19/89 |

| | Back. Conc. (ppt) | Spike Level (ppt) | Percent Recovery | PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 85 | 300 | 108 | 89 |
| 1,2,3,7,8-PeCDD | ND(2.9)a | 750 | 76 | 67 |
| 1,2,3,4,7,8-HxCDD | ND(4.5) | 750 | 76 | 93 |
| 1,2,3,4,6,7,8-HpCDD | 32 | 750 | 76 | 110 |
| OCDD | 665 | NA | NA | NA |
| 2,3,7,8-TCDF | 220 | 750 | 76 | 92 |
| 1,2,3,7,8-PeCDF | 4.9 | 750 | 74 | NA |
| 1,2,3,4,7,8-HxCDF | ND(2.5) | 750 | 121 | NA |
| 1,2,3,4,6,7,8-HpCDF | ND(4.3) | 750 | 87 | NA |
| OCDF | 22 | NA | NA | NA |

a--ND designates "not detected" above the minimum detectable concentration.
The number in parenthesis is the detection limit.

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | | MILL B | | | MILL C | | | MILL D | | | MILL F | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Final effluent water | | | Final effluent | | | Effluent | | | Effluent | | | Secondary Treated Mill Efflu | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/24/89 | | | 06/24/89 | | | 06/24/89 | | | 06/24/89 | | | 06/24/89 | | |
| Analytes | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 42[28%]a | 0.78 | | 89[23%]a | 0.76 | | ND(11)b | NA | | 86[35%]a | 0.74 | | 12 | 0.69 | |
| non-2,3,7,8-TCDD | ND(3.0)b | NA | | 101 | NA | | ND(11) | NA | | 34 | NA | | 138 | NA | |
| 13C-TCDD | | | 28 | | | 23 | | | 48 | | | 35 | | | 43 |
| 1,2,3,7,8-PeCDD | ND(6.6)[3 | NA | | ND(13)b[27%]c | NA | | ND(2.8) | NA | | ND(7.8)b | NA | | ND(8.8)b | NA | |
| non-2,3,7,8 sub PeCDD | 15 | NA | | 19 | NA | | 9.6 | NA | | 50 | NA | | 130 | NA | |
| 13C-PeCDD | | | 32 | | | 27 | | | 62 | | | 43 | | | 54 |
| 1,2,3,4,7,8-HxCDD | ND(12)[23 | NA | | ND(12)[19%]c | NA | | ND(6.6) | NA | | ND(9.3)[33%]c | NA | | D(12)[39%]c | NA | |
| 1,2,3,6,7,8-HxCDD | ND(12) | NA | | ND(12) | NA | | ND(6.6) | NA | | ND(9.3) | NA | | ND(24) | NA | |
| 1,2,3 7,8,9-HxCDD | ND(12) | NA | | ND(12) | NA | | ND(6.6) | NA | | ND(11) | NA | | ND(23) | NA | |
| non-2,3,7,8 sub HxCDD | ND(12) | NA | | ND(12) | NA | | ND(6.6) | NA | | 43 | NA | | 360 | NA | |
| 13C-HxCDD | | | 23 | | | 19 | | | 41 | | | 33 | | | 39 |
| 1,2,3,4,6,7,8-HpCDD | 170[18%]c | 0.96 | | 170[14%]c | 1.00 | | 120[29%]c | 1.05 | | 190[27%]c | 1.02 | | 260[30%]c | 1.01 | |
| non-2,3,7,8 sub HpCDD | 120 | NA | | 120 | NA | | 80 | NA | | 120 | NA | | 160 | NA | |
| 13C-HpCDD | | | 18 | | | 14 | | | 29 | | | 27 | | | 30 |
| OCDD | 4600[8%]c | 0.86 | | 3900[5%]c | 0.87 | | 2100[10%]c | 0.86 | | 3000[10%]c | 0.86 | | 2600[10%]c | 0.87 | |
| 13C-OCDD | | | 8 | | | 5 | | | 10 | | | 10 | | | 10 |
| 2,3,7,8-TCDF | 120[34%]a | 0.74 | | 160[26%]a | 0.80 | | 12 | 0.85 | | 200[39%]a | 0.77 | | 24 | 0.77 | |
| non-2,3,7,8-TCDF | 270 | NA | | 370 | NA | | 43 | NA | | 420 | NA | | 126 | NA | |
| 13C-TCDF | | | 34 | | | 26 | | | 56 | | | 39 | | | 51 |
| 1,2,3,7,8-PeCDF | ND(7.0) | NA | | ND(7.2) | NA | | ND(2.2) | NA | | ND(7.2) | NA | | 5.5 | 1.42 | |
| 2,3,4,7,8-PeCDF | ND(8.1) | NA | | ND(6.3) | NA | | ND(2.2) | NA | | ND(6.2) | NA | | 9.5 | 1.39 | |
| non-2,3,7,8 sub PeCDF | 30 | NA | | 21 | NA | | ND(2.2) | NA | | 28 | NA | | 49 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(5.2) | NA | | ND(6.2) | NA | | ND(5.8) | NA | | ND(4.8) | NA | | ND(14) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(5.2) | NA | | ND(6.2) | NA | | ND(5.8) | NA | | ND(4.8) | NA | | ND(7.1) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(5.2) | NA | | ND(6.2) | NA | | ND(5.8) | NA | | ND(4.8) | NA | | ND(8.2) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(5.2) | NA | | ND(6.2) | NA | | ND(5.8) | NA | | ND(4.8) | NA | | ND(2.5) | NA | |
| non-2,3,7,8 sub HxCDF | ND(5.2) | NA | | ND(6.2) | NA | | ND(5.8) | NA | | 20 | NA | | 54 | NA | |
| 1,2,3,4,6,7,8-HpCDF | ND(22) | NA | | ND(21) | NA | | ND(13) | NA | | 21 | 1.14 | | ND(23) | NA | |
| 1,2,3,4,7,8,9-HpCDF | ND(22) | NA | | ND(17) | NA | | ND(13) | NA | | ND(6.4) | NA | | ND(23) | NA | |
| non-2,3,7,8 sub HpCDF | 35 | NA | | ND(21) | NA | | ND(13) | NA | | 79 | NA | | 36 | NA | |
| OCDF | 140 | 0.82 | | 250 | 0.87 | | 78 | 0.95 | | 300 | 0.87 | | 110 | 0.90 | |

a--Internal standard recoveries were below the QA/QC objective of a minimum 40 percent.

b--ND designates "not detected" above the minimum detectable concentration
The number in parenthesis is the detection limit.

c--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in [] is the internal standard recovery.

| MILL E Effluent CAL ANALYTICAL 06/24/89 | | | MILL G Effluent CAL ANALYTICAL 06/24/89 | | | MILL H Effluent CAL ANALYTICAL 06/24/89 | | | MILL H DUPLICATE Effluent CAL ANALYTICAL 06/24/89 | | | MILL I Treated 2nd Effluent CAL ANALYTICAL 06/24/89 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 92 | 0.73 | | 31[38%]a | 0.72 | | 98[31%]a | 0.70 | | 64 | 0.79 | | 22[34%]a | 0.76 | |
| 108 | NA | | 34 | NA | | 122 | NA | | 96 | NA | | 14 | NA | |
| | | 56 | | | 38 | | | 31 | | | 41 | | | 34 |
| ND(18)b | NA | | ND(9.6)b | NA | | ND(13)b[ | NA | | ND(2.9)b | NA | | ND(25)b[20%]c | NA | |
| ND(18) | NA | | ND(9.6) | NA | | ND(13) | NA | | 22 | NA | | ND(25) | NA | |
| | | 40 | | | 51 | | | 19 | | | 48 | | | 20 |
| ND(17) | NA | | ND(19)[30%]c | NA | | ND(23)[2 | NA | | D(6.6)[31%]c | NA | | ND(12)[30%]c | NA | |
| ND(17) | NA | | ND(19) | NA | | ND(23) | NA | | ND(17) | NA | | ND(12) | NA | |
| ND(17) | NA | | ND(19) | NA | | ND(23) | NA | | ND(13) | NA | | ND(12) | NA | |
| ND(17) | NA | | 80 | NA | | 42 | NA | | 60 | NA | | ND(12) | NA | |
| | | 63 | | | 30 | | | 28 | | | 31 | | | 30 |
| 77 | 0.94 | | 270[22%]c | 1.05 | | 260[22%] | 0.92 | | 140[23%]c | 1.00 | | 170[23%]c | 1.05 | |
| 73 | NA | | 160 | NA | | ND(27) | NA | | 90 | NA | | 130 | NA | |
| | | 64 | | | 22 | | | 22 | | | 23 | | | 23 |
| 1000[33%]c | 0.84 | | 4300[8%]c | 0.85 | | 4200[8%] | 0.86 | | 2700[9%]c | 0.86 | | 2700[9%]c | 0.91 | |
| | | 33 | | | 8 | | | 8 | | | 9 | | | 9 |
| 840 | 0.78 | | 72 | 0.80 | | 420 | 0.77 | | 270 | 0.79 | | 74 | 0.82 | |
| 1460 | NA | | 128 | NA | | 450 | NA | | 390 | NA | | 126 | NA | |
| | | 77 | | | 46 | | | 44 | | | 43 | | | 45 |
| 36 | 1.47 | | ND(3.4) | NA | | ND(22) | NA | | ND(3.3) | NA | | ND(4.3) | NA | |
| 33 | 1.34 | | ND(3.4) | NA | | ND(22) | NA | | ND(4.4) | NA | | ND(4.3) | NA | |
| 71 | NA | | ND(3.4) | NA | | ND(22) | NA | | 24 | NA | | ND(13) | NA | |
| ND(19) | NA | | ND(15) | NA | | ND(9.4) | NA | | ND(2.0) | NA | | ND(8.4) | NA | |
| ND(9.0) | NA | | ND(15) | NA | | ND(9.4) | NA | | ND(2.0) | NA | | ND(8.4) | NA | |
| ND(9.0) | NA | | ND(15) | NA | | ND(9.4) | NA | | ND(2.6) | NA | | ND(8.4) | NA | |
| ND(9.0) | NA | | ND(15) | NA | | ND(9.4) | NA | | ND(2.0) | NA | | ND(8.4) | NA | |
| 31 | NA | | ND(15) | NA | | ND(9.4) | NA | | 14 | NA | | 7.6 | NA | |
| 44 | 1.18 | | 32 | 1.07 | | ND(41) | NA | | ND(19) | NA | | ND(23) | NA | |
| ND(14) | NA | | ND(12) | NA | | ND(41) | NA | | ND(5.4) | NA | | ND(23) | NA | |
| 31 | NA | | 78 | NA | | 76 | NA | | 33 | NA | | 49 | NA | |
| 190 | 0.94 | | 240 | 0.83 | | 320 | 0.87 | | 160 | 0.84 | | ND(180) | NA | |

Quality Assurance Data Summary
Precision Data
Field Duplicate

| | |
|---|---|
| Mill Code | MILL H |
| Matrix | Effluent |
| Laboratory | CAL ANALYTICAL |
| Laboratory Report Date | 06/24/89 |

| | #1 | | | #2 | | | |
|---|---|---|---|---|---|---|---|
| | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. REPORTED (ppq) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | Relative Percent Difference |
| 2,3,7,8-TCDD | 98[31%]a | 0.70 | | 64 | 0.79 | | 42 |
| non-2,3,7,8-TCDD | 122 | NA | | 96 | NA | | 24 |
| | | | 31 | | | 41 | |
| 1,2,3,7,8-PeCDD | ND(13)b[19 | NA | | ND(2.9)b | NA | | NA |
| non-2,3,7,8 sub PeCDD | ND(13) | NA | | 22 | NA | | NA |
| | | | 19 | | | 48 | |
| 1,2,3,4,7,8-HxCDD | ND(23)[28% | NA | | ND(6.6)[ | NA | | NA |
| 1,2,3,6,7,8-HxCDD | ND(23) | NA | | ND(17) | NA | | NA |
| 1,2,3,7,8,9-HxCDD | ND(23) | NA | | ND(13) | NA | | NA |
| non-2,3,7,8 sub HxCDD | 42 | NA | | 60 | NA | | 35 |
| | | | 28 | | | 31 | |
| 1,2,3,4,6,7,8-HpCDD | 260[22%]c | 0.92 | | 140[23%] | 1.00 | | 60 |
| non-2,3,7,8 sub HpCDD | ND(27) | NA | | 90 | NA | | NA |
| | | | 22 | | | 23 | |
| OCDD | 4200[8%]c | 0.86 | | 2700[9%] | 0.86 | | 43 |
| | | | 8 | | | 9 | |
| 2,3,7,8-TCDF | 420 | 0.77 | | 270 | 0.79 | | 43 |
| non-2,3,7,8-TCDF | 450 | NA | | 390 | NA | | 14 |
| | | | 44 | | | 43 | |
| 1,2,3,7,8-PeCDF | ND(22) | NA | | ND(3.3) | NA | | |
| 2,3,4,7,8-PeCDF | ND(22) | NA | | ND(4.4) | NA | | |
| non-2,3,7,8 sub PeCDF | ND(22) | NA | | 24 | NA | | |
| 1,2,3,4,7,8-HxCDF | ND(9.4) | NA | | ND(2.0) | NA | | |
| 1,2,3,6,7,8-HxCDF | ND(9.4) | NA | | ND(2.0) | NA | | |
| 2,3,4,6,7,8-HxCDF | ND(9.4) | NA | | ND(2.6) | NA | | |
| 1,2,3,7,8,9-HxCDF | ND(9.4) | NA | | ND(2.0) | NA | | |
| non-2,3,7,8 sub HxCDF | ND(9.4) | NA | | 14 | NA | | |
| 1,2,3,4,6,7,8-HpCDF | ND(41) | NA | | ND(19) | NA | | |
| 1,2,3,4,7,8,9-HpCDF | ND(41) | NA | | ND(5.4) | NA | | |
| non-2,3,7,8 sub HpCDF | 76 | NA | | 33 | NA | | |
| OCDF | 320 | 0.87 | | 160 | 0.84 | | |

a--Internal standard recoveries were below the QA/QC objective of a minimum 40 percent.

b--ND designates "not detected" above the minimum detectable concentration
The number in parenthesis is the detection limit.

c--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The [illegible] standard recove

Quality Assurance Data Summary
Recovery Data

| | |
|---|---|
| Mill Code | MILL A |
| Matrix | Final effluent water |
| Laboratory | CAL ANALYTICAL |
| Laboratory Repo | 06/24/89 |

| | Back. Conc. (ppq) | Spike Level (ppq) | Percent Recovery | PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 42 | 120 | 90 | 28 |
| 1,2,3,7,8-PeCDHD(6.6)b | | 300 | 73 | 20 |
| 1,2,3,4,7,8-HxC | ND(12) | 300 | 83 | 34 |
| 1,2,3,4,6,7,8-H | 170 | 300 | 50 | 35 |
| OCDD | NA | NA | NA | 24 |
| 2,3,7,8-TCDF | 120 | 300 | 63 | 38 |
| 1,2,3,7,8-PeCDFND(7.0) | | 300 | 70 | NA |
| 1,2,3,4,7,8-HxCND(5.2) | | 300 | 107 | NA |
| 1,2,3,4,6,7,8-H | ND(22) | 300 | 67 | NA |
| OCDF | NA | NA | NA | NA |

b--ND designates "not detected" above the minimum detectable concentration
The number in parenthesis is the detection limit.

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | | MILL B | | | MILL C | | |
|---|---|---|---|---|---|---|---|---|---|
| Matrix | Softwood pulp | | | Washed D2 pulp | | | Final pulp softwood line 2A | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/15/89 | | | 06/15/89 | | | 06/15/89 | | |
| Analytes | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 21 | 0.77 | | 5.9 | 0.77 | | 1.7 | 0.80 | |
| non-2,3,7,8-TCDD | 1.1 | NA | | ND(0.3)a | NA | | ND(0.3)a | NA | |
| 13C-TCDD | | | 72 | | | 80 | | | 55 |
| 1,2,3,7,8-PeCDD | 1.4 | 1.71 | | ND(0.3) | NA | | ND(0.4) | NA | |
| non-2,3,7,8 sub PeCDD | 1.0 | NA | | 0.3 | NA | | ND(0.4) | NA | |
| 13C-PeCDD | | | 63 | | | 65 | | | 72 |
| 1,2,3,4,7,8-HxCDD | ND(0.6)a | NA | | ND(0.2) | NA | | ND(0.5) | NA | |
| 1,2,3,6,7,8-HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | |
| 1,2,3,7,8,9-HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | |
| non-2,3,7,8 sub HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | |
| 13C-HxCDD | | | 83 | | | 89 | | | 66 |
| 1,2,3,4,6,7,8-HpCDD | 3.4 | 1.06 | | 2.3 | 1.03 | | 2.3 | 0.99 | |
| non-2,3,7,8 sub HpCDD | 3.6 | NA | | 2.0 | NA | | 1.9 | NA | |
| 13C-HpCDD | | | 88 | | | 97 | | | 62 |
| OCDD | 60 | 0.83 | | 28 | 0.84 | | 33[37%]b | 0.81 | |
| 13C-OCDD | | | 58 | | | 67 | | | 37 |
| 2,3,7,8-TCDF | 57 | 0.79 | | 15 | 0.80 | | 2.8 | 0.76 | |
| non-2,3,7,8-TCDF | 102 | NA | | 39 | NA | | 4.6 | NA | |
| 13C-TCDF | | | 78 | | | 87 | | | 59 |
| 1,2,3,7,8-PeCDF | 2.4 | 1.67 | | 2.4 | 1.63 | | ND(0.2) | AN | |
| 2,3,4,7,8-PeCDF | 1.5 | 1.32 | | 1.1 | 1.57 | | ND(0.2) | NA | |
| non-2,3,7,8 sub PeCDF | 8.8 | NA | | 4.2 | NA | | 1.7 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(0.4) | NA | | ND(1.2) | NA | | ND(0.4) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(0.1) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(0.4) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(0.1) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| non-2,3,7,8 sub HxCDF | 1.7 | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| 1,2,3,4,6,7,8-HpCDF | ND(0.6) | NA | | 0.8 | 1.13 | | ND(0.3) | NA | |
| 1,2,3,4,7,8,9-HpCDF | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| non-2,3,7,8 sub HpCDF | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| OCDF | ND(2.8) | NA | | 2.2 | 0.77 | | 1.9 | 0.92 | |

| Mill Code | MILL C | | | MILL D | | |
|---|---|---|---|---|---|---|
| Matrix | Final pulp hardwood line 3 | | | Pulp | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/15/89 | | | 06/15/89 | | |
| Analytes | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 0.4 | 0.65 | | 6.8 | 0.74 | |
| non-2,3,7,8-TCDD | ND(0.3)a | NA | | ND(0.5)a | NA | |
| 13C-TCDD | | | 81 | | | 66 |
| 1,2,3,7,8-PeCDD | ND(0.1) | NA | | ND(0.1) | NA | |
| non-2,3,7,8 sub PeCDD | ND(0.1) | NA | | ND(0.1) | NA | |
| 13C-PeCDD | | | 108 | | | 60 |
| 1,2,3,4,7,8-HxCDD | ND(0.2) | NA | | ND(0.6) | NA | |
| 1,2,3,6,7,8-HxCDD | ND(0.2) | NA | | ND(0.6) | NA | |
| 1,2,3,7,8,9-HxCDD | ND(0.2) | NA | | ND(0.6) | NA | |
| non-2,3,7,8 sub HxCDD | ND(0.2) | NA | | ND(0.6) | NA | |
| 13C-HxCDD | | | 87 | | | 95 |
| 1,2,3,4,6,7,8-HpCDD | 2.6 | 1.04 | | 3.3 | 0.92 | |
| non-2,3,7,8 sub HpCDD | 2.2 | NA | | 2.8 | NA | |
| 13C-HpCDD | | | 82 | | | 88 |
| OCDD | 41 | 0.88 | | 43 | 0.93 | |
| 13C-OCDD | | | 49 | | | 50 |
| 2,3,7,8-TCDF | 1.4 | 0.66 | | 19 | 0.80 | |
| non-2,3,7,8-TCDF | 2.7 | NA | | 38 | NA | |
| 13C-TCDF | | | 84 | | | 79 |
| 1,2,3,7,8-PeCDF | ND(0.1) | NA | | ND(0.6) | NA | |
| 2,3,4,7,8-PeCDF | ND(0.1) | NA | | ND(0.2) | NA | |
| non-2,3,7,8 sub PeCDF | 4.8 | NA | | 3.8 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(0.2) | NA | | ND(0.3) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(0.2) | NA | | ND(0.3) | NA | |
| non-2,3,7,8 sub HxCDF | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,4,6,7,8-HpCDF | ND(0.4) | NA | | ND(2.1) | NA | |
| 1,2,3,4,7,8,9-HpCDF | ND(0.4) | NA | | ND(2.1) | NA | |
| non-2,3,7,8 sub HpCDF | 1.0 | NA | | ND(2.1) | NA | |
| OCDF | 2.1 | 0.90 | | ND(3.0) | NA | |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

b--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in [] is the internal standard recovery.

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | | MILL B | | | MILL C | | | MILL C | | | MILL D | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Softwood pulp | | | Washed D2 pulp | | | Final pulp softwood line 2A | | | Final pulp hardwood line 3 | | | Pulp | | |
| Laboratory | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | | CAL ANALYTICAL | | |
| Laboratory Report Date | 06/15/89 | | | 06/15/89 | | | 06/15/89 | | | 06/15/89 | | | 06/15/89 | | |
| Analytes | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
| 2,3,7,8-TCDD | 21 | 0.77 | | 5.9 | 0.77 | | 1.7 | 0.80 | | 0.4 | 0.65 | | 6.8 | 0.74 | |
| non-2,3,7,8-TCDD | 1.1 | NA | | ND(0.3)a | NA | | ND(0.3)a | NA | | ND(0.3)a | NA | | ND(0.5)a | NA | |
| 13C-TCDD | | | 72 | | | 80 | | | 55 | | | 81 | | | 66 |
| 1,2,3,7,8-PeCDD | 1.4 | 1.71 | | ND(0.3) | NA | | ND(0.4) | NA | | ND(0.1) | NA | | ND(0.1) | NA | |
| non-2,3,7,8 sub PeCDD | 1.0 | NA | | 0.3 | NA | | ND(0.4) | NA | | ND(0.1) | NA | | ND(0.1) | NA | |
| 13C-PeCDD | | | 63 | | | 65 | | | 72 | | | 108 | | | 60 |
| 1,2,3,4,7,8-HxCDD | ND(0.6)a | NA | | ND(0.2) | NA | | ND(0.5) | NA | | ND(0.2) | NA | | ND(0.6) | NA | |
| 1,2,3,6,7,8-HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | | ND(0.2) | NA | | ND(0.6) | NA | |
| 1,2,3,7,8,9-HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | | ND(0.2) | NA | | ND(0.6) | NA | |
| non-2,3,7,8 sub HxCDD | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.5) | NA | | ND(0.2) | NA | | ND(0.6) | NA | |
| 13C-HxCDD | | | 83 | | | 89 | | | 66 | | | 87 | | | 95 |
| 1,2,3,4,6,7,8-HpCDD | 3.4 | 1.06 | | 2.3 | 1.03 | | 2.3 | 0.99 | | 2.6 | 1.04 | | 3.3 | 0.92 | |
| non-2,3,7,8 sub HpCDD | 3.6 | NA | | 2.0 | NA | | 1.9 | NA | | 2.2 | NA | | 2.8 | NA | |
| 13C-HpCDD | | | 88 | | | 97 | | | 62 | | | 82 | | | 88 |
| OCDD | 60 | 0.83 | | 28 | 0.84 | | 33(37%)b | 0.81 | | 41 | 0.88 | | 43 | 0.93 | |
| 13C-OCDD | | | 58 | | | 67 | | | 37 | | | 49 | | | 50 |
| 2,3,7,8-TCDF | 57 | 0.79 | | 15 | 0.80 | | 2.8 | 0.76 | | 1.4 | 0.66 | | 19 | 0.80 | |
| non-2,3,7,8-TCDF | 102 | NA | | 39 | NA | | 4.6 | NA | | 2.7 | NA | | 38 | NA | |
| 13C-TCDF | | | 78 | | | 87 | | | 59 | | | 84 | | | 79 |
| 1,2,3,7,8-PeCDF | 2.4 | 1.67 | | 2.4 | 1.63 | | ND(0.2) | AN | | ND(0.1) | NA | | ND(0.6) | NA | |
| 2,3,4,7,8-PeCDF | 1.5 | 1.32 | | 1.1 | 1.57 | | ND(0.2) | NA | | ND(0.1) | NA | | ND(0.2) | NA | |
| non-2,3,7,8 sub PeCDF | 8.8 | NA | | 4.2 | NA | | 1.7 | NA | | 4.8 | NA | | 3.8 | NA | |
| 1,2,3,4,7,8-HxCDF | ND(0.4) | NA | | ND(1.2) | NA | | ND(0.4) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,6,7,8-HxCDF | ND(0.1) | NA | | ND(0.3) | NA | | ND(0.4) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| 2,3,4,6,7,8-HxCDF | ND(0.4) | NA | | ND(0.3) | NA | | ND(0.4) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,7,8,9-HxCDF | ND(0.1) | NA | | ND(0.3) | NA | | ND(0.4) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| non-2,3,7,8 sub HxCDF | 1.7 | NA | | ND(0.3) | NA | | ND(0.4) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| 1,2,3,4,6,7,8-HpCDF | ND(0.6) | NA | | 0.8 | 1.13 | | ND(0.3) | NA | | ND(0.4) | NA | | ND(2.1) | NA | |
| 1,2,3,4,7,8,9-HpCDF | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.3) | NA | | ND(0.4) | NA | | ND(2.1) | NA | |
| non-2,3,7,8 sub HpCDF | ND(0.6) | NA | | ND(0.2) | NA | | ND(0.3) | NA | | 1.0 | NA | | ND(2.1) | NA | |
| OCDF | ND(2.8) | NA | | 2.2 | 0.77 | | 1.9 | 0.92 | | 2.1 | 0.90 | | ND(3.0) | NA | |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

b--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in () is the internal standard recovery

MILL E<br>Pulp<br>CAL ANALYTICAL<br>06/15/89 — MILL E DUPLICATE<br>Pulp<br>CAL ANALYTICAL<br>06/15/89 — MILL F<br>Pulp<br>CAL ANALYTICAL<br>06/15/89

| MILL E CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | MILL E DUPLICATE CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | MILL F CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|---|---|---|---|
| 7.4 | 0.73 | | 8.0 | 0.82 | | 7.4 | 0.80 | |
| ND(0.6)a | NA | | ND(0.6)a | NA | | ND(0.5)a | NA | |
| | | 72 | | | 76 | | | 50 |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| | | 66 | | | 117 | | | 44 |
| ND(0.5) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| ND(0.5) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| ND(0.5) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| ND(0.5) | NA | | ND(0.3) | NA | | ND(0.4) | NA | |
| | | 78 | | | 104 | | | 56 |
| 2.4 | 1.09 | | 5.3 | 0.97 | | 3.7 | 0.95 | |
| 2.1 | NA | | 4.0 | NA | | 3.2 | NA | |
| | | 84 | | | 93 | | | 57 |
| 40 | 0.83 | | 81 | 0.86 | | 47[36%]b | 0.89 | |
| | | 55 | | | 60 | | | 36 |
| 53 | 0.77 | | 51 | 0.78 | | 22 | 0.77 | |
| 148 | NA | | 140 | NA | | 37 | NA | |
| | | 72 | | | 86 | | | 52 |
| ND(0.7) | NA | | ND(0.6) | NA | | ND(0.3) | NA | |
| ND(0.6) | NA | | ND(0.4) | NA | | ND(0.3) | NA | |
| 17 | NA | | 3.1 | NA | | 2.2 | NA | |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2) | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2) | NA | | 1.1 | NA | | ND(0.3) | NA | |
| ND(0.1) | NA | | 0.6 | 1.17 | | ND(0.5) | NA | |
| ND(0.1) | NA | | ND(0.1) | NA | | ND(0.5) | NA | |
| ND(0.1) | NA | | 1.5 | NA | | ND(0.5) | NA | |
| 2.1 | 0.83 | | 4.1 | 0.85 | | 1.9 | 0.81 | |

MILL G<br>Washed D pulp, line A<br>CAL ANALYTICAL<br>06/15/89 — MILL H<br>Pulp<br>CAL ANALYTICAL<br>06/15/89 — MILL I<br>Line 1 Bleached Pulp<br>CAL ANALYTICAL<br>06/15/89

| MILL G CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | MILL H CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY | MILL I CONC. ODS (ppt) | ION RATIO | PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|---|---|---|---|
| 4.6 | 0.76 | | 124 | 0.81 | | 1.4 | 0.67 | |
| ND(0.4 | NA | | 7.0 | NA | | ND(0.2)a | NA | |
| | | 74 | | | 64 | | | 79 |
| 0.5 | 1.71 | | ND(1.5)a | NA | | ND(0.2) | NA | |
| ND(0.2 | NA | | 2.1 | NA | | ND(0.2) | NA | |
| | | 92 | | | 69 | | | 144 |
| 0.4 | 1.06 | | ND(0.2) | NA | | ND(0.4) | NA | |
| 0.7 | 1.12 | | 1.6 | 1.31 | | ND(0.4) | NA | |
| 0.5 | 1.15 | | ND(1.1) | NA | | ND(0.4) | NA | |
| 5.5 | NA | | 8.8 | NA | | 0.7 | NA | |
| | | 75 | | | 86 | | | 110 |
| 8.4 | 1.05 | | 3.6 | 1.01 | | 6.6 | 1.09 | |
| 8.4 | NA | | 2.8 | NA | | 6.2 | NA | |
| | | 69 | | | 85 | | | 98 |
| 65[38% | 0.83 | | 45 | 0.82 | | 81 | 0.89 | 62 |
| | | 38 | | | 47 | | | |
| 13 | 0.75 | | 716 | 0.78 | | 3.4 | 0.78 | |
| 21 | NA | | 810 | NA | | 3.8 | NA | |
| | | 76 | | | 43 | | | 101 |
| 0.7 | 1.46 | | 3.9 | 1.45 | | ND(0.2) | NA | |
| ND(0.2 | NA | | 4.7 | 1.53 | | ND(0.2) | NA | |
| 7.7 | NA | | 9.0 | NA | | ND(0.2) | NA | |
| 0.0 | 1.37 | | ND(0.6) | NA | | ND(0.3) | NA | |
| ND(0.2 | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| ND(0.2 | NA | | ND(0.4) | NA | | ND(0.3) | NA | |
| ND(0.2 | NA | | ND(0.2) | NA | | ND(0.3) | NA | |
| 0.9 | NA | | 1.6 | NA | | 0.4 | NA | |
| ND(1.2 | 1.13 | | 0.8 | 1.13 | | 0.7 | 1.05 | |
| ND(1.2 | NA | | ND(0.2) | NA | | ND(0.4) | NA | |
| 2.3 | NA | | ND(0.2) | NA | | 1.7 | NA | |
| 4.3 | 0.84 | | 2.3 | 0.89 | | 5.5 | 0.80 | |

Laboratory Duplicate

Mill Code MILL E
Matrix Pulp
Laboratory CAL ANALYTICAL
Laboratory Report Date 06/15/89

| | #1 CONC. ODS (ppt) | #1 ION RATIO | #1 PERCENT INTERNAL STANDARD RECOVERY | #2 CONC. ODS (ppt) | #2 ION RATIO | #2 PERCENT INTERNAL STANDARD RECOVERY | Relative Percent Difference |
|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | 7.4 | 0.73 | | 8.0 | 0.82 | | 7 |
| non-2,3,7,8-TCDD | ND(0.6)a | NA | | ND(0.6)a | NA | | NA |
| 13C-TCDD | | | 72 | | | 76 | |
| 1,2,3,7,8-PeCDD | ND(0.2) | NA | | ND(0.2) | NA | | NA |
| non-2,3,7,8 sub PeCDD | ND(0.2) | NA | | ND(0.2) | NA | | NA |
| 13C-PeCDD | | | 66 | | | 117 | |
| 1,2,3,4,7,8-HxCDD | ND(0.5) | NA | | ND(0.3) | NA | | NA |
| 1,2,3,6,7,8-HxCDD | ND(0.5) | NA | | ND(0.3) | NA | | NA |
| 1,2,3,7,8,9-HxCDD | ND(0.5) | NA | | ND(0.3) | NA | | NA |
| non-2,3,7,8 sub HxCDD | ND(0.5) | NA | | ND(0.3) | NA | | NA |
| 13C-HxCDD | | | 78 | | | 104 | |
| 1,2,3,4,6,7,8-HpCDD | 2.4 | 1.09 | | 5.3 | 0.97 | | 75 |
| non-2,3,7,8 sub HpCDD | 2.1 | NA | | 4.0 | NA | | 62 |
| 13C-HpCDD | | | 84 | | | 93 | |
| OCDD | 40 | 0.83 | | 81 | 0.86 | | 68 |
| 13C-OCDD | | | 55 | | | 60 | |
| 2,3,7,8-TCDF | 53 | 0.77 | | 51 | 0.78 | | 4 |
| non-2,3,7,8-TCDF | 148 | NA | | 140 | NA | | 6 |
| 13C-TCDF | | | 72 | | | 86 | |
| 1,2,3,7,8-PeCDF | ND(0.7) | NA | | ND(0.6) | | | NA |
| 2,3,4,7,8-PeCDF | ND(0.6) | NA | | ND(0.4) | | | NA |
| non-2,3,7,8 sub PeCDF | 17 | NA | | 3.1 | | | 138 |
| 1,2,3,4,7,8-HxCDF | ND(0.2) | NA | | ND(0.2) | | | NA |
| 1,2,3,6,7,8-HxCDF | ND(0.2) | NA | | ND(0.2) | | | NA |
| 2,3,4,6,7,8-HxCDF | ND(0.2) | NA | | ND(0.2) | | | NA |
| 1,2,3,7,8,9-HxCDF | ND(0.2) | NA | | ND(0.2) | | | NA |
| non-2,3,7,8 sub HxCDF | ND(0.2) | NA | | 1.1 | | | NA |
| 1,2,3,4,6,7,8-HpCDF | ND(0.1) | NA | | 0.6 | | | NA |
| 1,2,3,4,7,8,9-HpCDF | ND(0.1) | NA | | ND(0.1) | | | NA |
| non-2,3,7,8 sub HpCDF | ND(0.1) | NA | | 1.5 | | | NA |
| OCDF | 2.1 | 0.83 | | 4.1 | | | 65 |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

Quality Assurance Data Summary
Recovery Data

Mill Code MILL E
Matrix Pulp
Laboratory CAL ANALYTICAL
Laboratory Report 06/15/89

| | Back. Conc. (ppt) | Spike Level (ppt) | Percent Recovery | PERCENT INTERNAL STANDARD RECOVERY |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 7.3 | 25 | 107 | 73 |
| 1,2,3,7,8-PeCDD | ND(0.2)a | 150 | 67 | 68 |
| 1,2,3,4,7,8-HxCDD | ND(0.5) | 150 | 67 | 84 |
| 1,2,3,4,6,7,8-HpCD | 3.6 | 150 | 71 | 97 |
| OCDD | NA | NA | NA | 65 |
| 2,3,7,8-TCDF | 38 | 150 | 75 | 68 |
| 1,2,3,7,8-PeCDF | ND(0.7) | 150 | 80 | NA |
| 1,2,3,4,7,8-HxCDF | ND(0.2) | 150 | 107 | NA |
| 1,2,3,4,6,7,8-HpCD | 0.6 | 150 | 87 | NA |
| OCDF | NA | NA | NA | NA |

a--ND designates "not detected" above the minimum detectable concentratio The number in parenthesis is the detection limit.

SUMMARY OF RESULTS FOR THE ANALYSIS OF TETRA THROUGH OCTA DIOXINS AND FURANS

| Mill Code | MILL A | | MILL B | | MILL C | | MILL C | | MILL D | |
|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Softwood pulp | | Washed D2 pulp | | Final pulp softwood line 2A | | Final pulp hardwood line 3 | | Pulp | |
| Laboratory | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | |
| Laboratory Report Date | 06/15/89 | | 06/15/89 | | 06/15/89 | | 06/15/89 | | 06/15/89 | |
| Analytes | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) |
| 2,3,7,8-TCDD | 21 | 21 | 5.9 | 5.9 | 1.7 | 1.7 | 0.4 | 0.4 | 6.8 | 6.8 |
| non-2,3,7,8-TCDD | 1.1 | 0.011 | ND(0.3)a | 0 | ND(0.3)a | 0 | ND(0.3)a | 0 | ND(0.5)a | 0 |
| 1,2,3,7,8-PeCDD | 1.4 | 0.7 | ND(0.3) | 0 | ND(0.4) | 0 | ND(0.1) | 0 | ND(0.1) | 0 |
| non-2,3,7,8 sub PeCDD | 1.0 | 0.005 | 0.3 | 0.0015 | ND(0.4) | 0 | ND(0.1) | 0 | ND(0.1) | 0 |
| 1,2,3,4,7,8-HxCDD | ND(0.6)a | 0 | ND(0.2) | 0 | ND(0.5) | 0 | ND(0.2) | 0 | ND(0.6) | 0 |
| 1,2,3,6,7,8-HxCDD | ND(0.6) | 0 | ND(0.2) | 0 | ND(0.5) | 0 | ND(0.2) | 0 | ND(0.6) | 0 |
| 1,2,3,7,8,9-HxCDD | ND(0.6) | 0 | ND(0.2) | 0 | ND(0.5) | 0 | ND(0.2) | 0 | ND(0.6) | 0 |
| non-2,3,7,8 sub HxCDD | ND(0.6) | 0 | ND(0.2) | 0 | ND(0.5) | 0 | ND(0.2) | 0 | ND(0.6) | 0 |
| 1,2,3,4,6,7,8-HpCDD | 3.4 | 0.0034 | 2.3 | 0.0023 | 2.3 | 0.0023 | 2.6 | 0.0026 | 3.3 | 0.0033 |
| non-2,3,7,8 sub HpCDD | 3.6 | 0.000036 | 2.0 | 0.00002 | 1.9 | 0.000019 | 2.2 | 0.000022 | 2.8 | 0.000028 |
| OCDD | 60 | 0 | 28 | 0 | 33(37%)b | 0 | 41 | 0 | 43 | 0 |
| 2,3,7,8-TCDF | 57 | 5.7 | 15 | 1.5 | 2.8 | 0.28 | 1.4 | 0.14 | 19 | 1.9 |
| non-2,3,7,8-TCDF | 102 | 0.102 | 39 | 0.039 | 4.6 | 0.0046 | 2.7 | 0.0027 | 38 | 0.038 |
| 1,2,3,7,8-PeCDF | 2.4 | 0.24 | 2.4 | 0.24 | ND(0.2) | 0 | ND(0.1) | 0 | ND(0.6) | 0 |
| 2,3,4,7,8-PeCDF | 1.5 | 0.15 | 1.1 | 0.11 | ND(0.2) | 0 | ND(0.1) | 0 | ND(0.2) | 0 |
| non-2,3,7,8 sub PeCDF | 8.8 | 0.0088 | 4.2 | 0.0042 | 1.7 | 0.0017 | 4.8 | 0.0048 | 3.8 | 0.0038 |
| 1,2,3,4,7,8-HxCDF | ND(0.4) | 0 | ND(1.2) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| 1,2,3,6,7,8-HxCDF | ND(0.1) | 0 | ND(0.3) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| 2,3,4,6,7,8-HxCDF | ND(0.4) | 0 | ND(0.3) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| 1,2,3,7,8,9-HxCDF | ND(0.1) | 0 | ND(0.3) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| non-2,3,7,8 sub HxCDF | 1.7 | 0.00017 | ND(0.3) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| 1,2,3,4,6,7,8-HpCDF | ND(0.6) | 0 | 0.8 | 0.0008 | ND(0.3) | 0 | ND(0.4) | 0 | ND(2.1) | 0 |
| 1,2,3,4,7,8,9-HpCDF | ND(0.6) | 0 | ND(0.2) | 0 | ND(0.3) | 0 | ND(0.4) | 0 | ND(2.1) | 0 |
| non-2,3,7,8 sub HpCDF | ND(0.6) | 0 | ND(0.2) | 0 | ND(0.3) | 0 | 1.0 | 0.00001 | ND(2.1) | 0 |
| OCDF | ND(2.8) | 0 | 2.2 | 0 | 1.9 | 0 | 2.1 | 0 | ND(3.0) | 0 |
| TOTAL TOXICITY EQUIVALENCE | | 27.9 | | 7.8 | | 2.0 | | 0.6 | | 8.7 |
| PERCENTAGE OF TOTAL TOXICITY EQUIVALENCE FROM 2,3,7,8-TCDD AND 2,3,7,8-TCDF | | 96% | | 95% | | 100% | | 98% | | 99% |

| Mill Code | MILL F | | MILL E | | MILL E DUPLICATE | | MILL G | | MILL H | | MILL I | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | Pulp | | Pulp | | Pulp | | Washed D pulp, line A | | Pulp | | Line I Bleached Pulp | |
| Laboratory | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | | CAL ANALYTICAL | |
| Laboratory Report Date | 06/15/89 | | 06/15/89 | | 06/15/89 | | 06/15/89 | | 06/15/89 | | 06/15/89 | |
| Analytes | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) | CONC. ODS (ppt) | 2,3,7,8-TCDD Toxicity Equivalence (ppt) |
| 2,3,7,8-TCDD | 7.4 | 7.4 | 7.4 | 7.4 | 8.0 | 8 | 4.6 | 4.6 | 124 | 124 | 1.4 | 1.4 |
| non-2,3,7,8-TCDD | ND(0.5)a | 0 | ND(0.6)a | 0 | ND(0.6)a | 0 | ND(0.4)a | 0 | 7.0 | 0.07 | ND(0.2)a | 0 |
| 1,2,3,7,8-PeCDD | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | 0.5 | 0.25 | ND(1.5)a | 0 | ND(0.2) | 0 |
| non-2,3,7,8 sub PeCDD | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | 2.1 | 0.0105 | ND(0.2) | 0 |
| 1,2,3,4,7,8-HxCDD | ND(0.4) | 0 | ND(0.5) | 0 | ND(0.3) | 0 | 0.4 | 0.016 | ND(0.2) | 0 | ND(0.4) | 0 |
| 1,2,3,6,7,8-HxCDD | ND(0.4) | 0 | ND(0.5) | 0 | ND(0.3) | 0 | 0.7 | 0.028 | 1.6 | 0.064 | ND(0.4) | 0 |
| 1,2,3,7,8,9-HxCDD | ND(0.4) | 0 | ND(0.5) | 0 | ND(0.3) | 0 | 0.5 | 0.02 | ND(1.1) | 0 | ND(0.4) | 0 |
| non-2,3,7,8 sub HxCDD | ND(0.4) | 0 | ND(0.5) | 0 | ND(0.3) | 0 | 5.5 | 0.0022 | 8.8 | 0.00352 | 0.7 | 0.00028 |
| 1,2,3,4,6,7,8-HpCDD | 3.7 | 0.0037 | 2.4 | 0.0024 | 5.3 | 0.0053 | 8.4 | 0.0084 | 3.6 | 0.0036 | 6.6 | 0.0066 |
| non-2,3,7,8 sub HpCDD | 3.2 | 0.000032 | 2.1 | 0.000021 | 4.0 | 0.00004 | 8.4 | 0.000084 | 2.8 | 0.000028 | 6.2 | 0.000062 |
| OCDD | 47(36%)b | 0 | 40 | 0 | 81 | 0 | 65(38%)b | 0 | 45 | 0 | 81 | 0 |
| 2,3,7,8-TCDF | 22 | 2.2 | 53 | 5.3 | 51 | 5.1 | 13 | 1.3 | 716 | 71.6 | 3.4 | 0.34 |
| non-2,3,7,8-TCDF | 37 | 0.037 | 148 | 0.148 | 140 | 0.14 | 21 | 0.021 | 810 | 0.81 | 3.8 | 0.0038 |
| 1,2,3,7,8-PeCDF | ND(0.3) | 0 | ND(0.7) | 0 | ND(0.6) | 0 | 0.7 | 0.07 | 3.9 | 0.39 | ND(0.2) | 0 |
| 2,3,4,7,8-PeCDF | ND(0.3) | 0 | ND(0.6) | 0 | ND(0.4) | 0 | ND(0.2) | 0 | 4.7 | 0.47 | ND(0.2) | 0 |
| non-2,3,7,8 sub PeCDF | 2.2 | 0.0022 | 17 | 0.017 | 3.1 | 0.0031 | 7.7 | 0.0077 | 9.0 | 0.009 | ND(0.2) | 0 |
| 1,2,3,4,7,8-HxCDF | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | 0.6 | 0.006 | ND(0.6) | 0 | ND(0.3) | 0 |
| 1,2,3,6,7,8-HxCDF | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| 2,3,4,6,7,8-HxCDF | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.4) | 0 | ND(0.3) | 0 |
| 1,2,3,7,8,9-HxCDF | ND(0.3) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.2) | 0 | ND(0.3) | 0 |
| non-2,3,7,8 sub HxCDF | ND(0.3) | 0 | ND(0.2) | 0 | 1.1 | 0.00011 | 0.9 | 0.00009 | 1.6 | 0.00016 | 0.4 | 0.00004 |
| 1,2,3,4,6,7,8-HpCDF | ND(0.5) | 0 | ND(0.1) | 0 | 0.6 | 0.0006 | ND(1.2) | 0 | 0.8 | 0.0008 | 0.7 | 0.0007 |
| 1,2,3,4,7,8,9-HpCDF | ND(0.5) | 0 | ND(0.1) | 0 | ND(0.1) | 0 | ND(1.2) | 0 | ND(0.2) | 0 | ND(0.4) | 0 |
| non-2,3,7,8 sub HpCDF | ND(0.5) | 0 | ND(0.1) | 0 | 1.5 | 0.000015 | 2.3 | 0.000023 | ND(0.2) | 0 | 1.7 | 0.000017 |
| OCDF | 1.9 | 0 | 2.1 | 0 | 4.1 | 0 | 4.3 | 0 | 2.3 | 0 | 5.5 | 0 |
| TOTAL TOXICITY EQUIVALENCE | | 9.6 | | 12.9 | | 13.2 | | 6.3 | | 197.4 | | 1.8 |
| PERCENTAGE OF TOTAL TOXICITY EQUIVALENCE FROM 2,3,7,8-TCDD AND 2,3,7,8-TCDF | | 100% | | 99% | | 99% | | 93% | | 99% | | 99% |

a--ND designates "not detected" above the minimum detectable concentration. The number in parenthesis is the detection limit.

b--Internal standard recovery below 40 percent. Since there is no clear consensus in the scientific community as to what minimum should be required for the higher congeners, no minimum recovery criteria have been established. The number in [] is the internal standard recovery.

# APPENDIX F

## SUMMARY OF U.S. PAPER INDUSTRY 2378-TCDD/F DATA FOLLOWING COMPLETION OF 104 MILL STUDY - 1989-90

## I General

The following summarizes 'new data' provided to NCASI, EPA, and/or FDA following completion of the 104 Mill Study. In most cases, the sampling protocols outlined in the Study were followed. In general, companies also submitted QA/QC data to support these results. NCASI staff, however, have not reviewed the data submittals and have accepted the data at face value in compiling this summary. NCASI exercized some judgment in matching new data with corresponding 104 Mill Study results. It was not always possible to tell exactly which sample was repeated. In some cases, results or calculations based on the new data have been deleted (e.g. where both old and new data were non-detected, % reduction is not calculated).

Where calculations are made that include non-detected analytes, the absolute value of the detection limit is used to compute a percent reduction. This assumed calculation procedure produces a conservative estimate of the percent reduction for each vector.

## II. Summary By Export Vector

### A. Effluent Data

NCASI received new effluent data from 26 mills. These data are displayed in Figures F1A and F1B as old versus new. The "X" axis in this figure reflects mills ranked from high to low based upon the 104 Mill Study concentration. Some judgment was used in matching old data with new data. When new data was reported as non-detected without a specified detection limit, no percent reduction was calculated. Similarly, when both data sets were non-detected, no percent reduction was calculated.

Reductions ranked as high as 99 % for individual mills. Some mills with generally low 2378-TCDF results showed apparent, but probably meaningless, increases upon reanalysis. The data are summarized in Table F1. On average, mills with new data showed 64 % reduction for 2378-TCDD and 54 % for 2378-TCDF. On the basis of mass discharged with the effluent vector, expressed in milligrams per day (mg/d), these 26 mills accomplished a 79 % reduction in 2378-TCDD and 84 % in 2378-TCDF.

If the mass discharged in effluents from the 104 Mill Study is compared with the mass discharged reflected by the new data (mills with no new data are assumed to remain at the 104 Mill Study levels), the results show a 33 % reduction in 2378-TCDD discharged and a 50 % reduction in 2378-TCDF. Clearly, mills with "high" values in the 104 Mill Study data base tend to dominate the new data set. These data are shown in Table F1 as "Whole Industry Basis".

B. Pulp Data

New data (Figure F2) were reported for 50 bleach lines, representing nearly 1/3 of those in the 104 Mill Study. As was the case for effluents, some mills achieved very high percent reductions in both 2378-TCDD and 2378-TCDF. It is likely that these large reductions reported for some mills are due to changes in defoamer use.

Individual reductions in 2378-TCDD and 2378-TCDF concentrations summarized in Table F2 averaged 79 % and 81 %, respectively. On a mass basis, the reductions were similar: 81 % for 2378-TCDD and 90 % for 2378-TCDF. On a whole industry basis (i.e. lines with no new data assumed at the 104 Mill Study), the reductions were 39 % for 2378-TCDD and 51 % for 2378-TCDF.

C. Sludge Data

New data was reported for 26 mills and shown in Figure F3. In a few cases, 104 Mill Study data were for undewatered sludges and new data were for dewatered sludges. These cases were deleted from the data base. The largest reductions were again dramatic and exceeded 98 % for both 2378-TCDD and 2378-TCDF. The individual mill reductions reported in Table F3 averaged 67 % for 2378-TCDD and 60 % for 2378-TCDF. On a mass basis, these reductions were 85 % for 2378-TCDD and 88 % for 2378-TCDF. On a whole industry basis (as defined previously), the reductions were 39 % for 2378-TCDD and 53 % for 2378-TCDF.

TABLE F1 PERCENT REDUCTIONS IN EFFLUENTS

| BASIS | 2378-TCDD (%) | 2378-TCDF (%) |
|---|---|---|
| Mill Average | 64 | 52 |
| Mass Average | 79 | 84 |
| Whole Industry | 45 | 59 |

TABLE F2 PERCENT REDUCTIONS IN PULPS

| BASIS | 2378-TCDD (%) | 2378-TCDF (%) |
|---|---|---|
| Mill Average | 78 | 81 |
| Mass Average | 81 | 90 |
| Whole Industry | 46 | 52 |

TABLE F3 PERCENT REDUCTIONS IN SLUDGES

| BASIS | 2378-TCDD ( % ) | 2378-TCDF ( % ) |
| --- | --- | --- |
| Mill Average | 67 | 60 |
| Mass Average | 84 | 88 |
| Whole Industry | 37 | 56 |

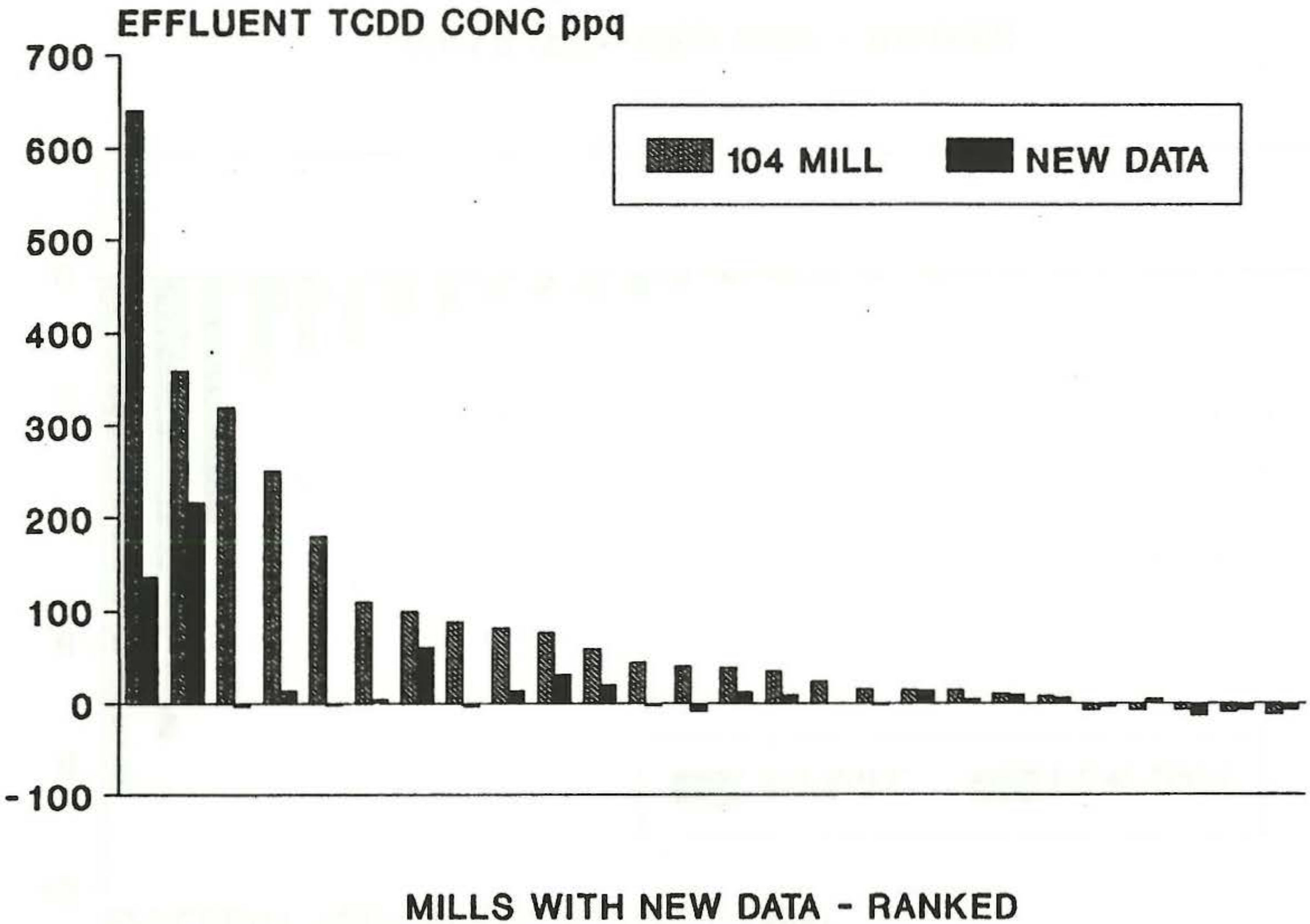



FIGURE F1A COMPARISON OF 104 MILL STUDY EFFLUENT 2378-TCDD CONCENTRATIONS VS NEW DATA

-F4-

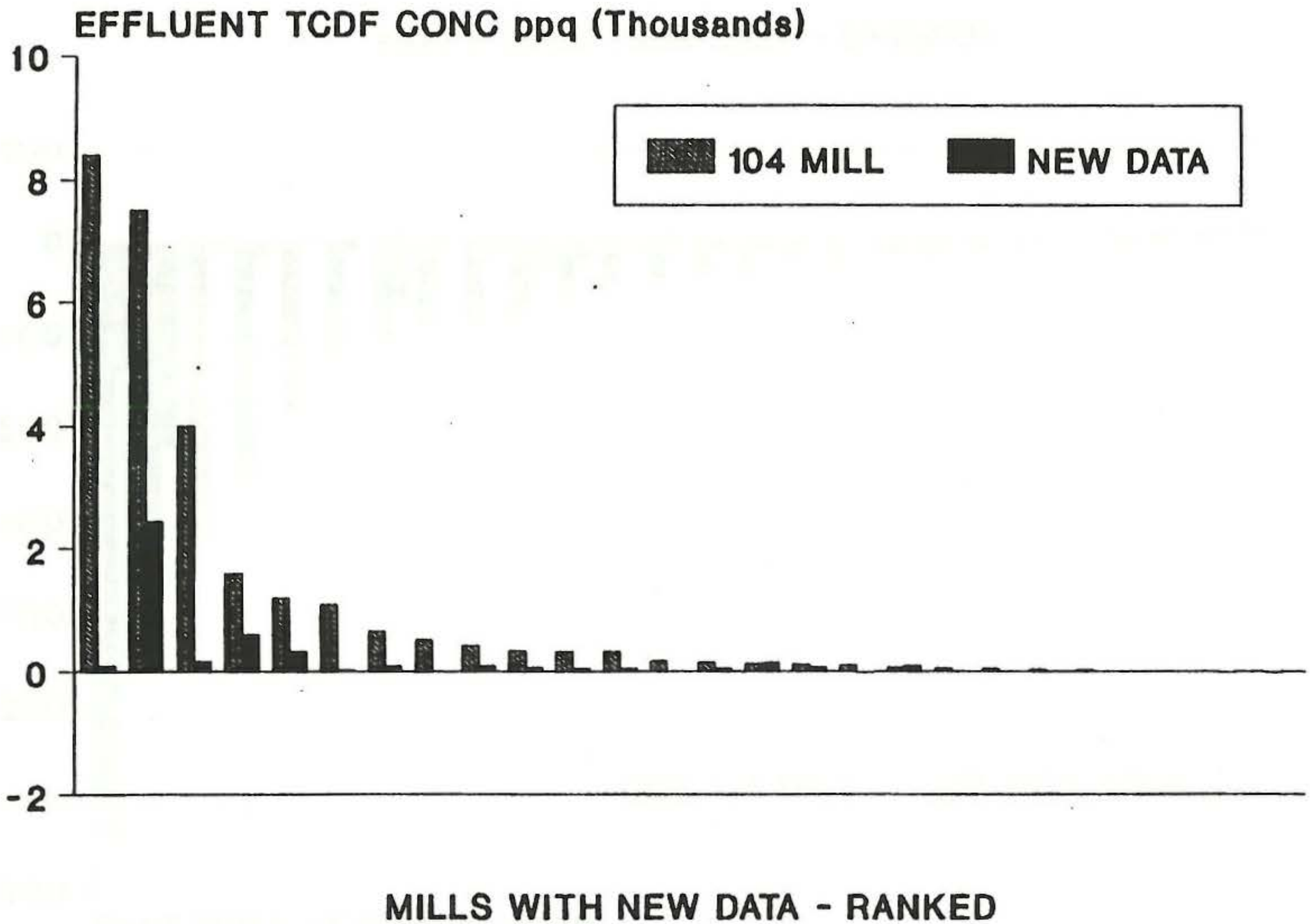



FIGURE F1B COMPARISON OF 104 MILL STUDY EFFLUENT 2378-TCDF CONCENTRATIONS VS NEW DATA

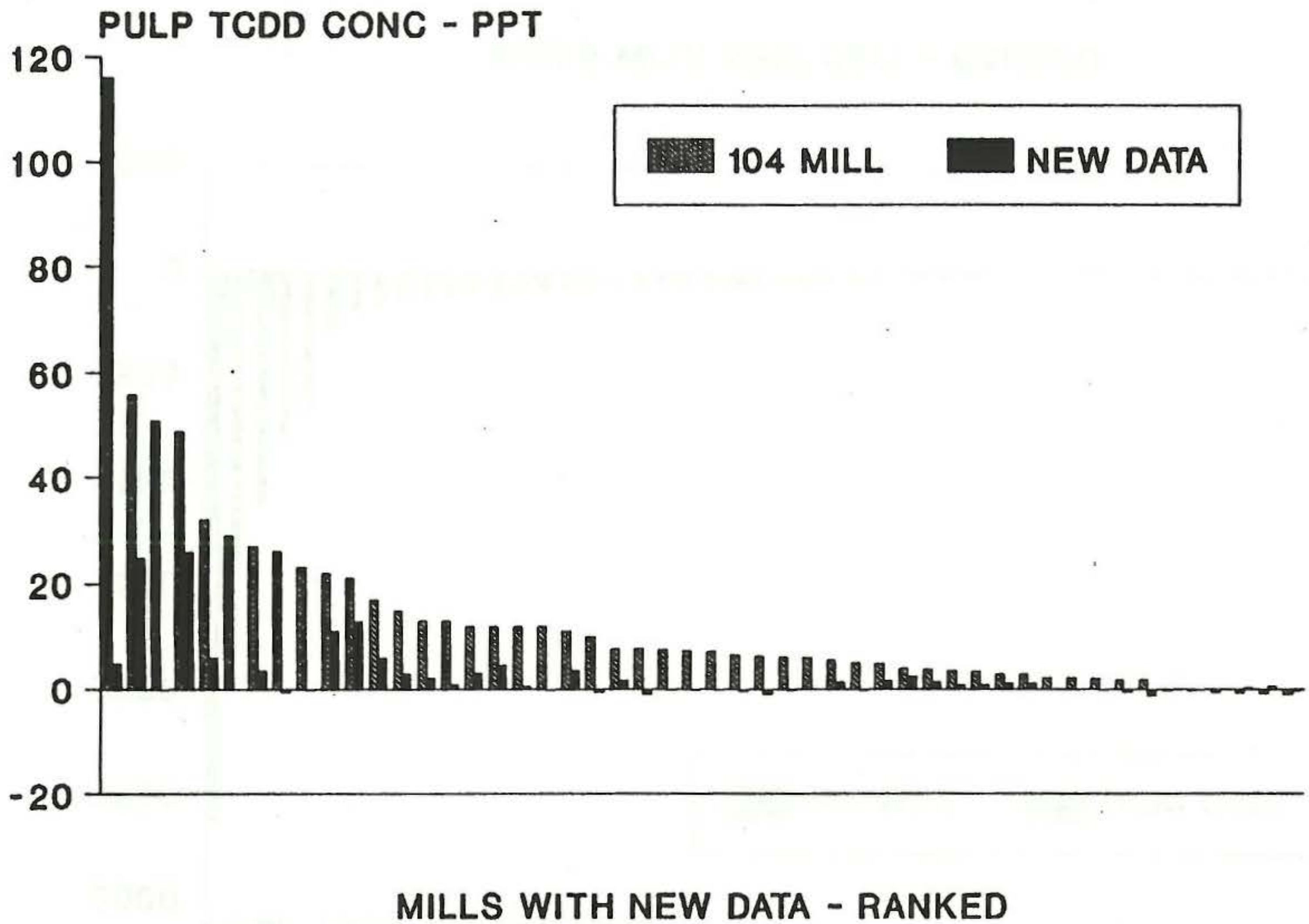



FIGURE F2A COMPARISON OF 104 MILL STUDY PULP 2378-TCDD CONCENTRATIONS VS NEW DATA

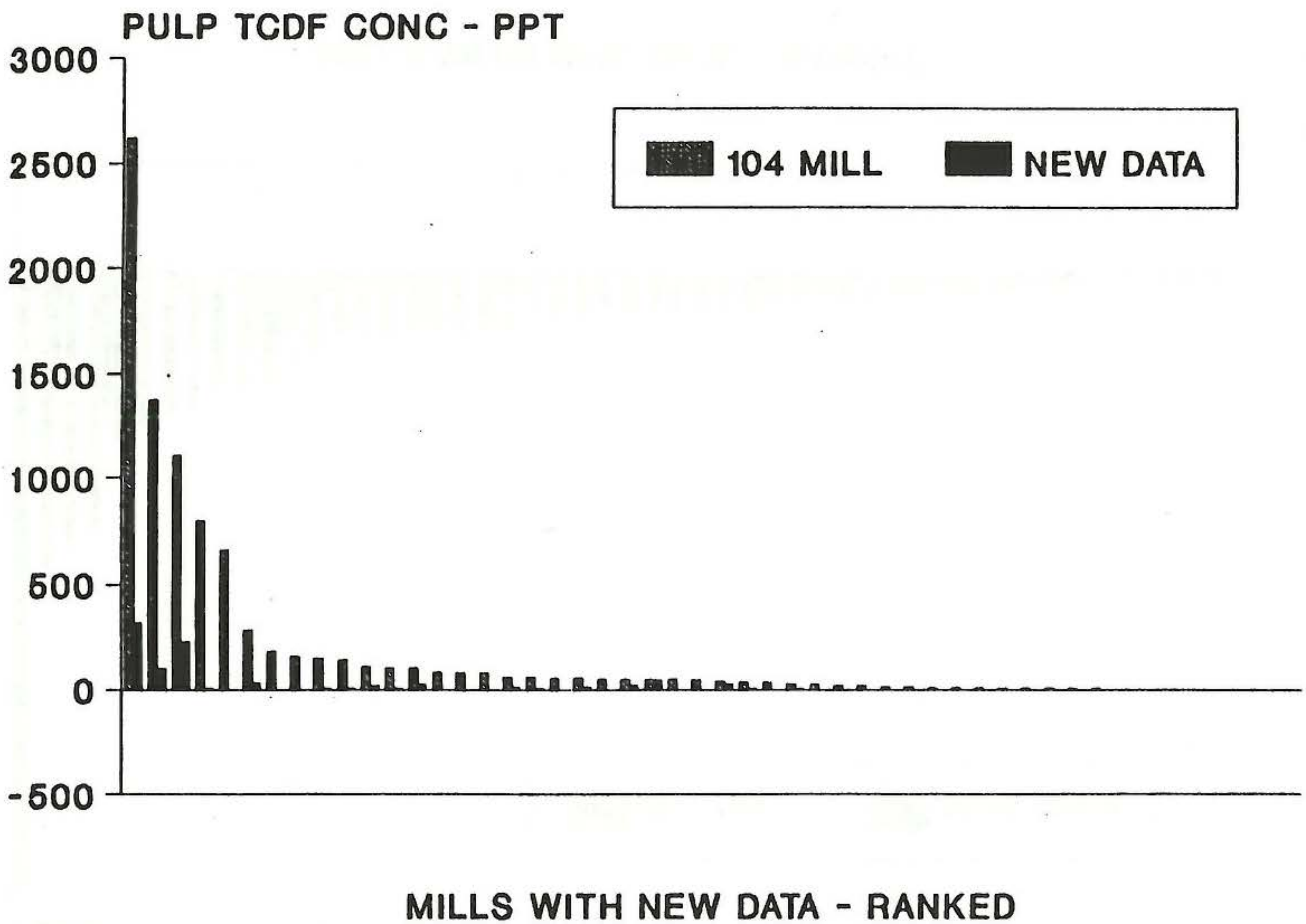



FIGURE F2B COMPARISON OF 104 MILL STUDY PULP 2378-TCDF CONCENTRATIONS VS NEW DATA

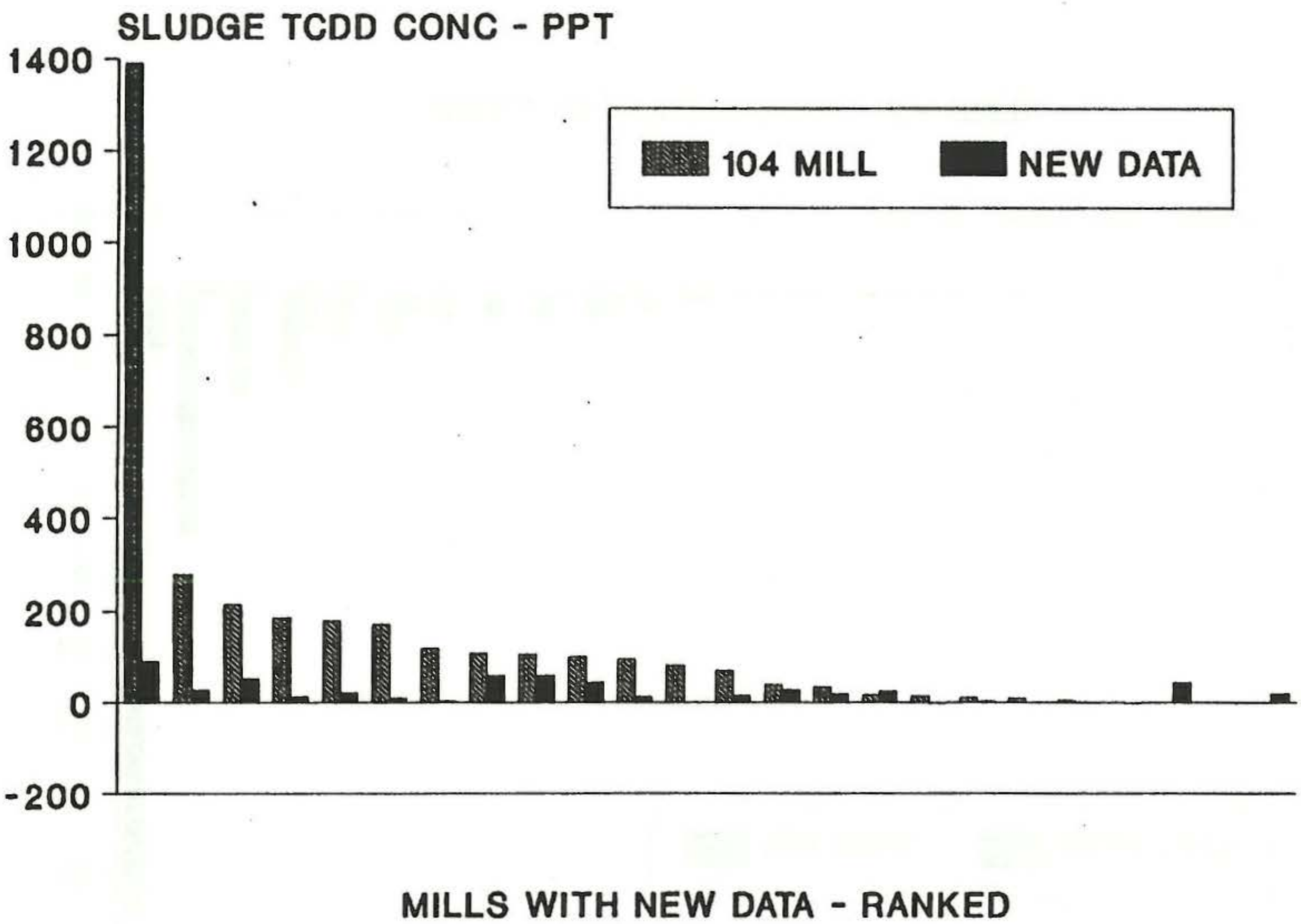



FIGURE F3A COMPARISON OF 104 MILL STUDY SLUDGE 2378-TCDD CONCENTRATIONS VS NEW DATA

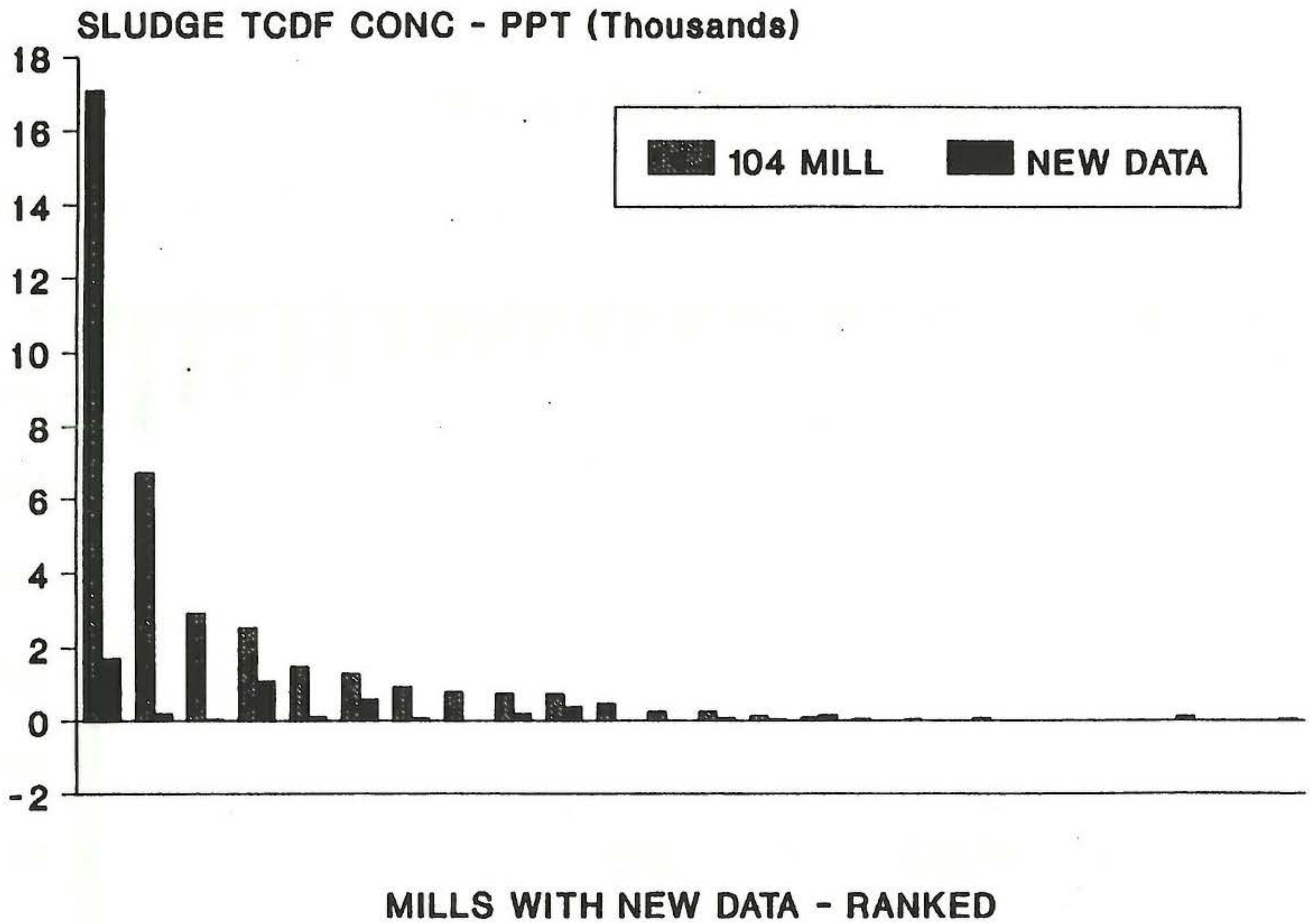



FIGURE F3B COMPARISON OF 104 MILL STUDY SLUDGE 2378-TCDF CONCENTRATIONS VS NEW DATA